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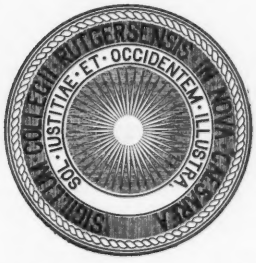

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SOIL SCIENCE

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A STUDY OF THE FERTILITY OF THE SOILS OF GREECE

GEORGE BOUYOUCOS

Michigan Agricultural Experiment Station

Received for publication May 12, 1921

INTRODUCTION

The soils of Greece are supposed to be among the oldest in the world. They have been under cultivation for long periods of time probably measured by many thousands of years. A large majority of them have never received any commercial fertilizers or green manure and very little, if any, animal manure. The productivity of most of these soils is at present quite low—the average yield of wheat for instance, is only about 11 bushels to the acre, and this yield is produced only once every two or three years. The system of farming that most farmers follow consists of cropping the land one year and leaving it idle, or fallow, one or two years.

For these and other reasons a knowledge of the state of productivity together with the chemical composition of these soils becomes at once of deep interest and great importance. Because of their great age and neglected fertility probably few other soils in the world present so interesting and profitable a case for study and comparison as those in Greece. Many of our present ideas and theories concerning soil fertility find an excellent basis for examination and testing in the soils of Greece.

In this paper are presented some results of study of these soils. This study was conducted by the late Cyril G. Hopkins (with the writer as his assistant) who was sent to Greece by the American Red Cross and the War Board at the special request of the Greek Government to investigate the soils of that country with the main object in view of increasing their productivity. The results of this investigation formed the basis and subject matter of a report which was published and addressed to the farmers and the Government of Greece. This report has not as yet been published in English but it is the intention of the University of Illinois to do so. This report, however, was intended primarily for the Greek farmers and consequently it is presented in a popular and didactic form. Because it was intended for the Greek farmers it does not include much scientific data and many observations and facts which are of value and interest to foreign and scientific readers. It is without doubt that had Dr. Hopkins lived he would have prepared a special and more technical paper on his studies and observations of the soils of Greece, together with the fundamental lessons and conclusions they point to.

Since it was the rare good forture of the present writer to be the associate and companion of Dr. Hopkins in all of his work in Greece, he has been asked and urged by interested students of soils and soil fertility to prepare a special article embodying the essential results of the investigation on the soils of Greece. He has deemed it advisable, and has undertaken to do this with all credit and honor to Dr. Hopkins.

In the investigation of the soils of Greece four different methods were pursued: (1) personal examination, (2) chemical analyses, (3) pot-culture experiments and (4) field experiments. In this paper will be presented briefly the most essential and important findings of all four methods.

Before the experimental results are presented, however, it is considered advisable for a more intelligent and thorough understanding of them to give a brief and general description of the soils of Greece, particularly as to their topography, geology, texture, management, climate, etc. Only the most essential facts which have a bearing on the experimental results and conclusions will be considered.

TOPOGRAPHY

Greece is a very mountainous country, more than half of the area consisting of mountains. The agricultural land is situated on plateaus or broad mountain tops of mountain ranges, on gradual slopes of high mountains, on hills and ridges, on river and inter-mountain valleys, on basins, valley deltas, piedmont slopes, inter-mountain and coastal plains. The number of large plains is small and these are found mainly in Thessaly, Macedonia and Thrace. There are few in Peloponnesus but they are not so extensive in area. A large portion of the agricultural land of the country is located on hills and rock mountains. Big mountains more than a thousand feet high, very steep and rocky, are being farmed. The land on the slopes of these mountains is actually made by the farmers themselves. They make patches of land by digging out the rocks or cultivating between the rocks. In order to keep the soil from being washed away these mountains are terraced with stone walls. The farmers abandon beautiful valleys and plains and go to farm these rock mountains because their soils are newer and more productive.

On account of the mountainous and hilly nature of the country, and in view of the fact that the rainfall comes usually in torrents, much erosion and gullying takes place on the agricultural land. These erosion and gullying processes are considerably facilitated by the fine texture of the soil.

GEOLOGY

Besides being very mountainous, Greece is also a very rocky country. Solid rock, probably, composes most of the mountains and hills. On account of their steepness and deforestation many of these mountains and hills are little else than barren rocks. These rocks are mainly limestone. In a few

places they consist of schists, shales, granites, conglomerates and sandstones, but the main and predominant rock formation of the country, or outcrop, is limestone. This limestone is remarkable for its uniformly high purity. In about 50 samples collected from different parts of the country and analyzed, the relative purity ranged from about 90 to 100 per cent with most samples showing about 98 per cent calcium carbonate.

The greatest portion of the soils of Greece, therefore, have been derived from limestone rock and they are the residue of the impurities of the limestone, or of the decomposed limestone itself, as large areas of land consist mostly of decomposed limestone rock or marl.

GEOLOGICAL CLASSIFICATION OF THE SOILS

Probably all the soils of Greece will come under the following standard classification:

Sedentary
- Residual
- Cumulose

Transported
- Colluvial and alluvial
- Marine and lacustrine
- Aeolian

It will be noted from this classification that there are no glacial soils in Greece, otherwise all the above formations are represented to a more or less extent. In extent of area the alluvial soils probably rank first followed perhaps, in order, by the residual, lacustrine, marine, colluvial, cumulose and aeolian soils.

Texture of Soils

On account of the rocky nature and rough configuration of the country one would think that the agricultural land in Greece would be very stony. On the contrary, nearly all of the land in the large plains, valleys, basins, and plateaus is entirely, or almost free of stones and gravel. The agricultural land, however, on most of the mountain slopes, on many of the hills, on some of the narrow valleys, small basins and mountain tops, and on nearly all of the piedmont slopes is quite stony or gravelly. The greatest majority of the soils of Greece are of fine texture, consisting of clays,silts, and loams. There are practically no pure sandy soils in Greece. Even on most of the mountain tops, mountain slopes and hills where stones and boulders are very abundant the fine earth consists usually of clay. This fine texture of the soils may be partly indicative of their long age.

ANNUAL RAINFALL

Although Greece is a very small country, having a territory of only about 50,000 square miles (not including the new territory acquired in the Great War) its annual rainfall varies greatly between the different sections. In some of the islands and part of the mainland in the western part of old Greece the rainfall is about 46 inches while in the region around Athens it is only about 13 inches. In the greatest part of the country, however, the average annual precipitation is considerably above 20 inches.

The periodic distribution of the rainfall in almost the entire country is very unfortunate. The greatest portion of it comes in the winter months and very little, if any, in the summer months. It usually starts about October and continues until March or April with most of it falling during November, December and January. The late spring months and all of the summer months are usually very dry. In some years and in certain sections of the country there may be no rainfall at all for four or five months in succession during the warmer part of the year.

It is readily evident, therefore, that insufficient and improper distribution of rainfall must be a very serious limiting factor in the crop production of Greece.

CROPS GROWN AND THEIR YIELDS

Nearly all of the common crops are grown in Greece to a greater or less extent. Of the cereal crops wheat is the most widely cultivated followed in order of importance by corn, barley, oats, mixture of wheat and barley, rye, millet, sorghum and rice. The average yield per acre of these crops in old Greece for the year 1914 is shown in table 1.

TABLE 1

Average yield per acre of the different crops grown in old Greece in 1914

NAME OF CROP	YIELD PER ACRE
	bushels
Wheat	11.2
Wheat and barley (mixture)	11.8
Corn	18.0
Barley	16.4
Oats	19.6
Rye	11.8
Millet	12.3
Sorghum	11.0
Rice	12.0

These yields, as has already been stated, are produced mostly once every two years.

The cultivated leguminous crops grown in Greece consist almost entirely of those species that are used for human food including beans, lentils, haricots, chickpeas, peas, etc. Practically no cultivated soil improving legumes such as clover and alfalfa are grown in Greece. This is due primarily to the severely dry summers.

One of the leading and most important agricultural industries is grape, raisin, olive and citrus culture. The large areas of land devoted to these fruits were not, however, included in the investigation and consequently will not be considered in this paper.

NEGLECTED SOIL FERTILITY

One of the most neglected factors in Greek agriculture is the fertility of the soil. The farmers as a whole have done practically nothing to maintain or increase the fertility of the soil. The great majority of them have never used any commercial fertilizers on their land, and as previously stated, practically no cultivated soil-improving legumes are employed. Even the legumes which they grow for human food are usually pulled out by the roots, and so utilized that the soils derive practically no benefit from them in the way of nitrogen enrichment.

There are, however, growing on most of the agricultural land, different kinds of wild annual legumes. But on account of the frequent and close grazing by the sheep, and on account of the early and long drought, they are usually not allowed to attain any significant development. The soils during their idleness, however, probably receive some nitrogen from these wild legumes.

Farm manure is quite scarce in Greece. This is due to the fact that the chief livestock consist of sheep and goats which graze most of the time on the mountains. The only manure, therefore, that most of the agricultural land ever receives, is from the sheep and goats during grazing, and this is negligible.

CHEMICAL COMPOSITION OF THE SOILS

More than eighty samples of soils were collected from different parts of Greece representing nearly all of the most extensive and important soil types and areas of the country, and were analyzed for the total elements of nitrogen, phosphorus, potassium, magnesium and calcium, and also for limestone and acidity. For the determination of total nitrogen, phosphorus, potassium, magnesium and calcium the old "American official method" (1) was used; for the determination of the limestone and acidity, or limestone requirement, the Hopkin's Method (1, 2) was employed. The adjoining tables show the total quantities of these substances in 2,000,000 pounds of fine dry soil, and also a descriptive record of all the soils collected and analyzed. All the soils have been arranged in groups according to the regions from which they were taken.

TABLE 2

Description of soil samples

SOIL NUMBER	TOWN NEARBY	TOPOGRAPHY OF LAND	AGRICULTURAL CONDITION	CHARACTER OF SOIL	RESULTS OF ANALYSES						
					Weight of elements in an acre of 2,000,000 lbs. of air-dry soil					Limestone in an acre of 2,000,000 lbs.	Lime requirement
					Nitrogen	Phosphorus	Potassium	Magnesium*	Calcium*		
					lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	
1	Thebes	Valley slope, nearly level	Grain	Sandy clay loam	3,100	760	7,140			117,400	
2	Larissa	Hill land, rolling	Grain	Gravelly loam	2,640	650	21,560			421,400	
3	Larissa	Upland valley, nearly level	Grain	Clay	1,790	740	34,800			48,800	
4	Lamia	Valley slope, nearly level	Grain	Silt loam	2,070	1,060	25,790			76,200	
5	Lianokladi Junction	Hill land, sloping	Grain	Gravelly clay	1,870	730	13,240			160,400	
6	Arbanitsa	Piedmont, gently sloping	Grain	Clayey silt	2,610	1,680	45,300			43,000	
7	Pylos	Valley, nearly level	Grain	Calcareous clay	3,190	1,810	34,830			205,800	
8S	Gargalianoi	Plateau, nearly level	Abandoned	Subsoil clay	1,750	740	27,910	14,170	5,990		930
9	Sageika	Coastal plain, undulating	Grain	Sandy loam	1,420	1,090	16,760	3,850	6,060		60
10S	Sageika	Coastal plain, undulating	Grain	Subsoil of 9, clay	1,490	1,410	24,470	5,480	4,070		100
11S	Sageika	Coastal plain, undulating	Grain	Subsoil, clay	1,020	1,180	18,360	6,750	9,970		340

* Soils which contained much limestone were not analyzed for calcium or magnesium.

12	Lappa	Coastal plain, nearly level	Waste land, brush	Sandy clay loam	1,460	210	14,900	3,540	5,290		80
13S	Lappa	Coastal plain, nearly level	Waste land, brush	Subsoil of 11, sandy clay	1,180	530	16,730	6,600	8,490		90
14	Likochia	Mountain slope, terraced	Grain	Stony clay	5,180	2,450	43,280	18,560	22,060	23,100	
15S	Megalopolis	Ridge land, rolling	Waste land, brush	Subsoil, clay	1,780	1,250	30,910	10,290	7,860		770
16S	Imbraim	Ridge land, rolling	Waste land, weeds	Subsoil, clay	1,750	1,170	23,620	8,210	5,720		140
17	Larissa	Upland valley, nearly level	Grain	Clay (pot culture)	2,650	1,050	36,700	15,620	19,510	2,200	
18	Thebes	Valley slope, nearly level	Grain	Sandy loam (pot cultures)	3,040	1,220	10,150	46,150	42,650	86,200	
19	Sageika	Coastal plain, undulating	Grain	Sandy loam (pot cultures)	2,880	460	16,290	5,620	5,050		70
20	Sageika	Coastal plain, nearly level	Grain	Sandy loam (field experiments)	2,270	1,110	22,270	5,050	6,070		100
21	Gargalianoi	Plateau, undulating	Abandoned	Silty clay	2,870	1,020	20,880	8,920	13,900		170
22S	Gargalianoi	Plateau, undulating	Abandoned	Subsoil of 21, clay	1,770	840	24,950	15,430	12,060		6,030
23	Gargalianoi	Plateau, nearly level	Abandoned	Silty clay (culture experiments)	3,480	1,450	19,440	6,800	14,800		70
24	Kalabryta	Mountain slope, terraced	Grain	Silty clay	3,720	2,050	31,920	15,340	127,140	266,000	
25	Bysoka	Valley delta, nearly level	Grain	Gravelly sandy clay	3,960	1,410	23,180	7,430	6,210	6,300	

TABLE 2—*Continued*

SOIL NUMBER	TOWN NEARBY	TOPOGRAPHY OF LAND	AGRICULTURAL CONDITION	CHARACTER OF SOIL	RESULTS OF ANALYSES						
					Weight of elements in an acre of 2,000,000 lbs. of air-dry soil					Limestone in an acre of 2,000,000 lbs.	Lime requirement
					Nitrogen	Phosphorus	Potassium	Magnesium*	Calcium*		
					lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	
26	Megalopolis	Hill land, steep slope	Partly abandoned	Clayey silt	4,360	1,450	40,940			421,800	
27	Megalopolis	Ridge land, nearly level	Abandoned, scrub trees	Silt loam	3,410	380	16,770	5,220	5,980		70
28S	Megalopolis	Ridge land, nearly level	Abandoned, scrub trees	Subsoil of 27, clay	1,720	1,020	21,850	7,010	11,710		970
29	Megalopolis	Ridge land, undulating	Partly abandoned	Gravelly silt loam	1,990	1,320	20,370	6,160	10,690		970
30S	Megalopolis	Ridge land, undulating	Partly abandoned	Subsoil of 29, clay	1,990	1,020	27,580	8,090	2,930		50
31S	Mpilali	Ridge land, rolling	Abandoned, scrub trees	Subsoil, clay	2,320	620	38,820	20,590	7,390		13,550
32	Armeni, Crete	Valley, nearly level	Grain or fallow	Sandy silt loam	2,860	300	24,190	11,930	4,330		50
33	Armeni, Crete	Mountain slope, terraced	Grain	Calcareous clay loam	5,770	4,890	25,350			713,200	
34	Chania, Crete	Valley, gentle slope	Grain or fallow	Sandy clay loam	2,270	710	18,690	6,050	2,900		50
35S	Chania, Crete	Valley, gentle slope	Grain or fallow	Subsoil of 34, sandy clay	2,290	1,020	33,170	6,730	2,900		50
36	Souda, Crete	Mountain top, rolling	Grain	Clay	4,290	1,840	39,020	15,200	9,490	4,300	
37	Knosos, Crete	Mountain top, rolling	Grain or idle	Calcareous loam	3,130	910	13,150			1,487,400	
38	Candia, Crete	Valley, nearly level	Grain or vines	Loam	2,270	1,110	22,290			630,800	
39	Phinika, Crete	Ridge land, rolling	Grain	Calcareous loam	3,430	1,430	25,470			860,400	

40	Korytsa	Low valley, nearly level	Grain or meadow	Clayey silty loam	4,250	1,670	42,320			88,400	
41	Korytsa	Valley delta, steep slope	Grain or fallow	Sandy clay loam	2,310	1,240	19,000	7,360	43,520	1,900	
42	Korytsa	Hills or valley ridges	Grain or fallow	Clayey silt loam	2,320	1,450	47,200	12,400	22,460	11,800	
43	Yannina	Mountain top, rolling	Grain or fallow	Cherty clay	4,400	11,720	22,350			42,800	100
44	Soudovitra	Valley, gentle slope	Grain or fallow	Silty clay loam	2,900	3,520	32,200	10,980	16,000		100
45	Yannina	Ridge land, undulating	Pasture	Silt loam	2,320	1,830	22,060	6,450	9,440		530
46S	Yannina	Ridge land, undulating	Pasture	Subsoil of 45, clay	2,010	1,430	26,850	11,430	6,150		2,440
47	Keletron	Ridge land, undulating	Grain or fallow	Clayey sandy loam	2,280	1,010	30,660	1,760	4,180		50
48S	Keletron	Ridge land, undulating	Grain or fallow	Subsoil of 47, sandy clay	2,230	1,210	36,690	4,430	3,330		70
49	Keletron	Valley land, nearly level	Grain	Clay, very gummy	2,860	610	23,790	9,470	8,020		100
50S	Keletron	Valley land, nearly level	Grain	Subsoil of 49, clay	1,760	1,050	38,380	17,770	15,750		1,120
51	Kastoria	Mountain slope, terraced	Grain and vines	Clay loam	2,590	1,640	45,490			91,600	
52	Pella	Ridge land, undulating	Grain or idle	Clay loam	2,930	1,680	47,490			126,400	
53	Koutsopodi	Hill land, rolling	Grain or fallow	Calcareous silt loam	2,570	1,020	17,160			1,158,800	
54	Argos	Steep piedmont slope	Grain	Very strong clay loam	4,390	1,670	39,900			38,800	
55	Argos	Valley gentle slope	Grain	Stony sandy loam	2,280	1,530	26,680			97,400	

TABLE 2—*Concluded*

SOIL NUMBER	TOWN NEARBY	TOPOGRAPHY OF LAND	AGRICULTURAL CONDITION	CHARACTER OF SOIL	RESULTS OF ANALYSES						
					Weight of elements in an acre of 2,000,000 lbs. of air-dry soil					Limestone in an acre of 2,000,000 lbs.	Lime requirement
					Nitrogen	Phosphorus	Potassium	Magnesium*	Calcium*		
					lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	
56	Tatari	Hills or ridges, rolling	Grain or fallow	Silty clay loam	3,800	1,040	27,030			411,000	
57	Magoula	Valley, nearly level	Grain or fallow	Clay loam	3,000	750	35,410	17,510	26,830	4,800	
58	Pharsala	Valley, nearly level	Grain	Silty clay loam	4,160	2,550	26,810	45,230	43,710	12,600	
59	Lazarina	Plain, nearly level	Cotton	Silty clay loam	3,180	1,860	37,380	28,340	18,120	6,800	
60	Kapudji	Valley, nearly level	Grain or forage	Sandy silt loam	2,880	1,550	21,010	45,590	63,020	5,200	
61	Salonica	Hill land, rolling	Grain or fallow	Clayey silt loam	2,890	1,030	19,710			274,800	
62	Dobitsa	Mountain slope, terraced	Grain or fallow	Silty clay, stony	2,870	1,020	32,840			730,400	
63	Dobitsa	Hill land, rolling	Grain or fallow	Gravelly clayey loam	2,320	1,040	42,630			509,000	
64	Zichna	Ridge land, undulating	Grain or pasture	Clayey silt loam	2,040	1,660	57,210			85,200	
65	Serres	Valley, gentle slope	Grain or pasture	Sandy loam	1,700	2,020	64,490			88,200	
66	Drama	Piedmont slope, gentle	Grain or fallow	Clay loam	3,030	1,520	38,990	15,290	27,450	10,400	
67	Dokzat	Ridge land, undulating	Grain or fallow	Clayey sandy loam	1,840	810	30,440	3,100	5,060		70
68S	Dokzat	Ridge land, undulating	Grain or fallow	Subsoil of 67, clay	1,460	730	33,390	4,290	3,720		50
69	Philippi	Plain, nearly level	Abandoned	Sandy silt loam	1,990	410	38,430	3,420	10,300		50
70	Drama	Plain, nearly level	Abandoned	Clay	2,650	730	23,490	5,250	12,330		70

71	Boutianoi	Mountain slope	Grain or fallow	Shaly loam	2,280	1,220	45,050	15,560	6,530		70
72	Sparta	Hills and ridges	Grain or fallow	Calcareous loam	2,850	1,530	21,730			563,000	
73	Kamary	Mountain slope, terraced	Grain or fallow	Silty clay	4,100	1,880	39,930	15,140	23,610	9,400	
74	Tripolis	Hill land, rolling	Grain or fallow	Stony loam	2,570	1,430	32,750			81,800	
75	Tripolis	Valley, nearly level	Grain or forage	Silt loam	2,570	1,120	23,480	31,390	14,600		50
76	Liopesi	Piedmont slope	Grain or fallow	Very stony loam	3,160	2,050	32,220			201,600	
77	Marathon	Piedmont slope	Grain or idle land	Stony loam	4,020	1,540	36,850	17,550	28,580	5,200	
78	Marathon	Piedmont slope	Grain or fallow	Sandy loam	2,280	1,630	25,000			181,800	
79*	Marathon	Coastal plain, level	Rice or corn	Calcareous muck	6,540	670	2,520			719,500	
80S	Marathon	Coastal plain, level	Rice or corn	Subsoil of 79, calcareous clay	3,480	930	40,210			607,400	
81	Sageika	Coastal plain, level	Grain or pasture	Clay over marl	2,050	520	22,330	12,580	20,320	6,000	

* No. 79 is a muck soil and the weights reported are found in 1,000,000 pounds per acre, representing about $6\frac{3}{8}$ inches in depth.

The foregoing analytical data reveal many interesting and important facts. First of all they show that the soils of Greece differ very greatly in fertility as measured by chemical analysis. Thus nitrogen, in the plowed soil, varies from 1420 pounds per acre in soil no. 9 to 5770 pounds in soil no. 33. Out of 81 soils examined, 65 are surface soils. The nitrogen variation in these surface soils is shown in table 3.

Of the three soils which contain more than 5000 pounds of nitrogen, two came from among limestone rocks and terraces on the mountain slopes, and one from muck land; while of the eight soils which contain less than 2000 pounds, three came from level plains, two from valleys, one from hill land, and two from ridge land. Of the eight soils which contain an amount ranging between 4000 and 4500, two are located on piedmont slopes, two on mountain tops, one on a mountain slope, one on hill land, one in a valley, and one in a low valley. It seems evident, therefore, that most of the soils richest in nitrogen are found on mountain and piedmont slopes, while the soils poorest in nitrogen are generally located in level plains and in some of the large valleys.

TABLE 3

Nitrogen in surface soils

NITROGEN CONTENT	NUMBER OF SOILS WITHIN GROUP
lbs. per acre	
1500–2000	8
2000–2500	14
2500–3000	19
3000–3500	10
3500–4000	3
4000–4500	8
5000–6500	3

There are only 14 soils out of the 65 which contain more than 3500 pounds of nitrogen and 41 contain less than 3000 pounds. It appears, therefore, that most of the soils of Greece are either poor or very poor in nitrogen. Considering, however, that most of these soils have probably been farmed for many hundreds, if not thousands, of years, without any attempt to maintain or increase their nitrogen content, it is significant that they contain as much of this element as they do.

Only 8 out of 65 surface soils and none of the subsoils contain more than 2000 pounds of phosphorus. All of these soils are on mountain slopes or low mountain tops or near the foot of mountains. Three of these soils, no. 44, 58 and 65, are composed of material washed down from nearby mountains. The other quite similar mountain soils contain 1840 pounds in no. 36, 1640 pounds in no. 51, and 1880 pounds in no. 73. Other soils from piedmont slopes which seem comparable are no. 6,54,66 and 77; also no. 7 represents a deposit washed from nearby mountain regions. These soils contain between 1500 and 2000 pounds of phosphorus. Soils no. 26, 37 and 62, although hill and

mountain slopes, average nearly half limestone, which seems to account for their low phosphorus contents.

In general, soils which have been formed from recent decomposition of limestone, and do not still contain large amounts of limestone in the fine earth, are either rich in phosphorus or moderately well supplied. These are found among the limestone rocks on the mountains, on some piedmont slopes and in some valley deposits washed from such mountain regions. The more common soils of Greece, however, vary from poor to very poor in phosphorus. This is true of the great coastal and inland plains of the broad intermountain valleys and plateaus, and of the low hills and ridges. Most of the agriculturally abandoned lands are very poor in phosphorus. Of the five soils which contain less than 500 pounds of phosphorus three are situated on level plains, one in a valley and one on a level ridge land. Of the twelve soils whose phosphorus content varies from 500 to 1000 pounds five are located in valleys, three in plains, two on hill lands, one on a mountain top and one on ridge land.

TABLE 4

Phosphorus in surface soils

PHOSPHORUS CONTENT	NUMBER OF SOILS WITHIN GROUP
lbs. per acre	
200– 500	5
500–1000	12
1000–1500	23
1500–2000	17
2000–2500	4
2550	1
3520	1
4890	1
11,720	1

Potassium, though quite abundant, varies from 2500 pounds in soil 79 (muck) and 7,140 pounds in soil 1 to 64,490 pounds in no. 65. On the whole, all of the normal soils examined are well supplied with potassium and most of them are very rich in this element.

Magnesium ranges from 1760 pounds in soil no. 47 to 46,150 pounds in no. 18. Many of the soils contain a large amount of magnesium.

Calcium varies from only 2900 pounds in soil no. 34 to 127,140 pounds in no. 24. Soils which contained much limestone were not analyzed for calcium or magnesium. Such soils, of course, would indicate a greater amount of calcium than is shown in the maximum figure above.

Limestone ranges from none at all in several soils to 1,487,400 pounds in soil no. 37. Most of the soils of Greece are abundantly supplied with limestone.

The limestone requirement varies from none in most soils to 13,550 pounds in soil no. 31. The acid soils form a fairly large aggregate area and are scat-

tered in many widely separate regions. They are usually found on plains, ridges, hills, or plateaus, which have lost their original supply of limestone and which can not receive additional supplies washed down from higher lying lands. Of such soils included in this study, 15, 16 and 27–31 are situated on ridge lands near the center of a great valley; no. 8, 21, 22 and 23 are found on a plateau; no. 34 and 35 are situated on a sloping land in the center of a valley or coastal plain; no. 45 and 46 are found on low broad ridges in the center of a valley; no. 47 and 50 are located on ridge land and coastal plain across a lake; and no. 67–70 are found in a great plain.

Many soils were found abundantly supplied with limestone at a depth of 3 feet and more which, however, were very acid at the surface. Some of these subsoils testd as much as 50 per cent of calcium carbonate.

POT CULTURE TESTS

Although the time that the commission remained in Greece was only about a year, it managed to conduct a few pot culture and field tests. The object of these tests was to secure additional information and to verify, if possible, some of the analytical data. In the pot culture experiments, sweet clover was grown in 38 earthenware jars having a diameter of about 8 inches and a depth of about 10 inches. The following treatments, and combinations thereof, were used:

	gm.
Acid phosphate	6.000
Sodium chloride	2.975
Potassium chloride	3.730
Ground limestone (where needed)	150.000

The soils employed were no. 17, 18, 19 and 23. Each test was run in duplicate series, A and B. The sweet clover plants were allowed to grow for about three months when the tops were cut and weighed immediately (see tables 5 and 6).

An examination of these results shows that phosphorus produced a marked increase in yield in every case. Soils no. 18 and 17 both contained limestone, but where applied to acid soils no. 19 and 23, limestone gave a large increase in every case, whether applied alone or in addition to phosphorus and potassium.

After harvesting the sweet clover it was partially dried and mixed together with the roots into the soil, and millet planted. The nitrogen contained in the sweet clover turned under resulted in large growth by the millet over the check.

FIELD TESTS

Temporary field tests, eight in number, were inaugurated in different parts of Greece on soils representing typical and large areas. The underlying principle of all these experiments was to show the effect of phosphorus and

TABLE 5

Relative effects of phosphorus, sodium and potassium on soil not in need of lime

POT NUMBER	TREATMENT	WEIGHT OF GREEN TOPS OF CLOVER PLANTS				AVERAGE
		Soil number 17 from Larissa		Soil number 18 from Thebes		
		Series A	Series B	Series A	Series B	
		gm.	*gm.*	*gm.*	*gm.*	*gm.*
2	Nothing	38	41	30	18	32
3	Acid phosphate	95	108	104	112	105
4	Acid phosphate–NaCl	84	84	125	132	106
5	Acid phosphate–KCl	82	74	116	118	97

TABLE 6

Relative effect of phosphorus, sodium and potassium on soil in need of lime

POT NUMBER	TREATMENT	WEIGHT OF GREEN TOPS OF CLOVER PLANTS				AVERAGES	
		Soil number 19 from Sageika		Soil number 23 from Gargalianoi		Four pots	Eight pots
		Series A	Series B	Series A	Series B		
		gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
2	Nothing	19	25	10	4	14	
3	Ground limestone	63	39	23	22	37	34
4	Ground limestone, acid phosphate	76	67	71	62	69	87
5	Ground limestone, acid phosphate, NaCl	84	89	74	82	82	94
6	Acid phosphate, NaCl, KCl	85	90	72	80	82	90
7	Acid phosphate, KCl			30	28	29	

TABLE 7

Effect of acid phosphate and lime on growth of sweet clover

SOIL TREATMENT	YIELD PER ACRE OF DRY HAY	
	Soil 19, Sageika	Soil 23, Gargalianoi
	lbs.	*lbs.*
None, check	150	220
Limestone	740	850
Limestone, acid phosphate	3090	3150
Acid phosphate	310*	510

* Computed from later harvest.

lime on the growth of sweet clover, and in turn the beneficial influence of this when incroporated with the soil on the grain crops. In this paper the results of only two representative experiments will be presented. One of these experiments was conducted on soil 19 and the other on soil 23, both of which were also employed in the pot culture tests. Phosphorus was applied at the rate of about 800 pounds of acid phosphate, and limestone at the rate of about ten tons to the acre. The clover seed was planted on the field represented by soil 19 on January 10 and the crop was harvested on June 28, of the same year. On the field represented by soil 23 the seed was planted on January 15 and the crop was harvested on June 26. It must be remembered that both of these soils are acid. The yield of dry clover hay produced by the different treatments at each field is shown in table 7.

It will be readily seen that at both fields all the treatments caused a very marked increase in the yield of sweet clover. The greatest increase, however, occurred where both limestone and phosphate were applied.

In our travels through Greece it was observed that the soils of the country are very susceptible to fertilization, especially with phosphorus and nitrogen, and that acid soils are much improved by treatment with limestone.

SUMMARY

It is a matter of record that the average yield of grain crops in Greece is low and that the average yield of wheat is only about 11 bushels to the acre. These low yields are generally produced only once in two years because of the common practice of fallowing.

Three main factors are responsible for this low yield of grain crops. These are (1) poor and unclean seed and weedy stand of plants, (2) insufficient rainfall in the late spring and in the summer and (3) low content of the nitrogen and phosphorus in most of the common soils and the almost complete failure of the farmers to supply these elements to the soil in the form of fertilizers or manures.

There is no question that both of the first two factors, and especially the second, play a considerable rôle in limiting the yield of grain crops on the soils of Greece. But the chief limiting factor has been the loss of soil fertility. Where nitrogen and phosphorus are present in sufficient amounts, the soils were reported to produce fairly good crops even in dry seasons. On soils very low in these elements the crops were almost a failure in the dry season.

The chemical analysis of over 80 representative types of soils shows that the soils of Greece vary very greatly in fertility. Thus nitrogen, in an acre of 2,000,000 pounds of surface soil varies from 1500 to 5000 pounds; phosphorus from 210 to 11,720 pounds; potassium from 2520 to 64,490 pounds; magnesium from 1760 to 46,150 pounds; calcium from 2900 to 127,140 pounds; limestone from 0 to 1,487,400 pounds; and acidity from 0 to 12,550 pounds limestone equivalent.

With the exception of a few abnormal soils, all of the soils examined are well supplied with potassium.

Limestone is present in abundance in most of the soils of Greece. There are some soils, however, scattered in many widely separate regions, that contain no limestone and are acid. These are usually found on level plains, ridges, hills and plateaus, which have lost their original supply of limestone and which can not receive additional supplies washed down from high lying land. On the whole, however, acid soils in Greece are comparatively few.

It was found that many beautiful plains with soils of good physical conditions were agriculturally abandoned, because the new soils of the mountain slopes produce more profitable yields.

Chemical examination shows that the soils of these mountain slopes are usually richer both in nitrogen and phosphorus and especially in the latter, than those of the plains. The soils richest in nitrogen and phosphorus and usually the most productive, were found on the terraces of the mountain slopes, on the sides and bottoms of small valleys between hills, ridges or mountains and on the bottom of big valleys overflowed with river water. The poorest soils in nitrogen and phosphorus and usually the least productive, were found on level plateaus, tops of hills and ridges, and on some of the level plains which neither receive deposits by overflow nor lose partially depleted soil by erosion.

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THE NATURE OF CERTAIN ALUMINUM SALTS IN THE SOIL AND THEIR INFLUENCE ON AMMONIFICATION AND NITRIFICATION

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INTRODUCTION

That soluble salts of aluminum are present in acid soils in considerable quantities, and that these salts may be largely responsible for soil acidity, are conclusions that have been reached by several investigators. The literature on aluminum in its relation to soil acidity has been fully reviewed by Mirasol (10). No attempt, therefore, will be made in this paper to treat the subject historically, especially in view of the fact that the problem to be discussed deals in part with the influence of aluminum salts on bacterial activity, on which subject little work has been reported. References to the literature will be made from time to time as they bear directly upon the particular topic under discussion.

The toxicity of soluble aluminum salts toward farm crops has been clearly demonstrated by Hartwell and Pember (5), Abbott, Conner and Smalley (1), Mirasol (10), and by the writer in some preliminary work, which in view of its agreement with what has been reported, need not be considered further. There does not appear, however, to be such definite information regarding the effect of these salts upon the important bacterial processes of ammonification and nitrification. In view of the fact that the hydrolysis of the sulfate, chloride and nitrate of aluminum produces a strongly acid medium, it would be expected that the nitrifying organisms would be affected adversely by the presence of these salts in the soil. Furthermore, since it has been maintained by some investigators, and particularly by Mirasol, that the origin of soluble aluminum salts in the soil is for the most part to be ascribed to bacterial activity, it became desirable in planning this work to study this factor also.

[1] The successful termination of the work herein reported is due in no small measure to Dr. Albert L. Whiting, under whose supervision the investigation was carried out. It is the intention of Doctor Whiting to continue investigations on the problem of aluminum in its relation to soil bacteria and acidity, the results of which should contribute to a more complete understanding of the whole question of soil acidity.

THE NATURE OF CERTAIN ALUMINUM COMPOUNDS IN THE SOIL

Before attempting experimental work involving a study of bacterial activity as influenced by aluminum salts, it was deemed essential to investigate in some detail the exact nature of the aluminum compounds of the soil which might be involved in the problem under consideration. Merely to group all the aluminum compounds that might be extracted from the soil under a single head, namely, as being toxic to plant growth, seemed to be wholly unwarranted because of the widely differing nature of the aluminum compounds concerned. For this reason, it has been considered well to review very briefly the opinions that are held with respect to the character and origin of these compounds before entering into a discussion of the experimental work to be reported.

Theories on the formation of soluble aluminum in soils

Probably one of the first investigators to give attention to the presence of aluminum in the soil from the standpoint of soil acidity was Veitch (15). In his study of the Hopkins' method for the determination of soil acidity, he attributed the acidity of the soil extract to hydrolyzed aluminum salts which had been formed by the basic ion of the neutral salt solution used as an extractant in the determination, replacing the aluminum in alumino-silicates. Truog (14) holds much the same view, stating that the treatment of an acid mineral soil with a salt solution results in the exchange of an equivalent amount of iron and aluminum for the base taken up. The iron and aluminum go into solution as salts and since they are strongly hydrolyzed in solution, they enter into the titration much the same as an equivalent amount of acid. The conception that the presence of these salts is to be ascribed to true displacement by the basic ion of the salt solution receives further support, according to Truog, from the fact that acetates bring aluminum and iron into solution as well as salts of the stronger mineral acids. It is improbable, in his opinion, that the dilute acetic acid formed by removal of the base would dissolve iron and aluminum compounds to saturation.

A second theory to explain the presence of aluminum in neutral salt extracts of soil is that held by Parker (11), who assumes that aluminum is brought into solution by a side reaction of free acid formed by the removal of the basic ion of the salt solution by selective adsorption. Knight (9) takes much the same view, asserting, however, that the basic ion is removed to make up the deficiency of bases in the acid soil rather than by the physical adsorption. The mineral acid thus formed from the acid ion of the salt solution then attacks insoluble aluminum and brings it into solution as the salt of the mineral acid as is assumed by the replacement of bases theory. This is a very important point. It is the starting point of much of the work that will be reported later.

In addition to the two theories that have been mentioned to account for the rise of soluble aluminum compounds in the soil, attention should be

directed to a third, namely, the biochemical origin of soluble aluminum. Abbott, Conner, and Smalley (1) reported, in 1913, the presence of aluminum nitrate in a peat soil and attributed its rise to nitrification taking place in the absence of a more suitable base than aluminum. This idea has been developed recently by Mirasol. From the work by Ames and Boltz (2) it would appear that aluminum may be brought into solution also as the sulfate in the process of sulfofication.

There have been presented, then, three explanations of the existence of soluble aluminum in the soil: first, that it is brought into solution by replacement of bases from alumino-silicates; second, that it is produced by the action of acid formed by withdrawal of the base from a neutral salt solution; third that is has its origin in the normal processes of nitrification and sulfofication.

An understanding of which of these three processes actually occurs or whether they all take place in the soil, while of considerable value, is of secondary importance to a knowledge of the actual chemical compound into which aluminum enters and as which it exists in the soil solution. To illustrate, if aluminum salts of the mineral acids are constantly being produced in some acid soils, the theory that has now been fully accepted by many, that active aluminum is an important factor in acidity would appear to receive added confirmation. If, however, the soluble aluminum of the soil is present as the hydroxide, as the work of Knight indicates, and not as salts, then aluminum ceases to be the important factor that it is claimed to be and becomes no more than a measure of acidity, the actual cause of which lies much deeper, but which is as yet not understood.

The presence of soluble aluminum hydroxide in soil extracts

A review of the work of Knight may serve to bring out more clearly the point just mentioned. In his study of the Hopkins' method for soil acidity, Knight found that the aluminum present in the potassium nitrate extract of an acid soil was only slightly less than enough to account for the total acidity of the extract as measured by titration with standard alkali. Basing his reasoning on the work of Blum (3), who showed that aluminum hydroxide is completely precipitated before the hydrogen-ion concentration of the solution reaches pH=7, and, conversely, that it must pass into solution when the hydrogen-ion concentration rises above this value, Knight inferred that the aluminum which he determined in the extract was present as the hydroxide. The extract was then subjected to dialysis with the result that none of the aluminum contained within it diffused through the membrane; whereas three-fourths of the total acidity of the extract was found to have diffused. On neutralization of the contents of the collodion flasks, aluminum hydroxide was precipitated. The logical interpretation of the result of this experiment is that the aluminum extracted from the soil by a neutral salt solution is present not as the easily diffusible salt, the nitrate in this case, but as soluble aluminum hydroxide.

Additional support of this contention is provided by the investigations of Rose (12), from which it appears that precipitated aluminum hydroxide passes readily into the hydrosol condition in the presence of very weak acid, namely 4 per cent acetic acid and N/20 to N/35 hydrochloric or nitric acid. He explains this formation of hydrosols as being due to the forming of a series of hydrated oxides, those hydrates containing the largest number of molecules being produced first. In studying the solubility of aluminum hydroxide in acetic acid, Rose found that hydrates having the formulas $Al_2O_3 \cdot 7H_2O$ and $Al_2O_3 \cdot 6H_2O$ were produced first, swelling up and setting as gelatinous masses. With the addition of more acetic acid $Al_2O_3 \cdot 4H_2O$ to $Al_2O_3 \cdot 2.75\ H_2O$ formed, giving only weakly opalescent solutions. As soon as the degree of hydration passed below the last value with additional acid, a hydrosol no longer formed and normal aluminum acetate resulted.

It would seem, then, that this action of weak acids on aluminum hydroxide might easily explain the presence of soluble aluminum in the soil. The weak acid of the soil or the acid produced by the withdrawal of the basic ion from a salt solution reacts with colloidal aluminum hydroxide and produces a solution that is, to all intents and purposes, perfectly clear, but which contains aluminum in a form which will not pass through a semi-permeable membrane. That there are considerable quantities of aluminum hydroxide in soils is the conclusion reached by Mirasol so that there seems to be no reason why the conversion of aluminum hydrogels to hydrosols should not take place within the soil. It should be mentioned in this regard that, according to the work of Rose, the aluminum hydroxide need not be in the gelatinous condition, i.e., as when precipitated by ammonium hydroxide, in order to enter the sol state. Perfectly dry aluminum hydroxide will pass readily into the sol provided it has not been dried at too high a temperature. The application of this principle to soil conditions is, of course, that the hydroxide in the soil need not be in the plastic condition associated with wet clay in order to form the sol but it may be simply a finely divided powder. In summary, if this principle of the reversibility of aluminum hydrogels to hydrosols obtains within the soil, aluminum passes into the soil solution not as the diffusible salt of an acid but as the indiffusible hydroxide. Not only does this theory appear plausible but it offers a ready explanation for the fact that Knight was unable to bring about diffusion of aluminum from a collodion flask. The tendency, however, of increasing soil acidity would be eventually to convert aluminum hydroxide to soluble salts of aluminum.

Data from a totally different source tend toward substantiation of the theory that has just been proposed. Reference is made to the extremely large quantities of aluminum which Mirasol succeeded in leaching from three acid soils by extracting with potassium nitrate and water until the last portions of the percolate showed in each case no titratable acidity. After drying, the soils were analyzed for aluminum, the difference in the aluminum content of the leached and unleached soil being taken as the active aluminum normally to be

found in the soils. Table 1 has been compiled from the results of analysis as reported by Mirasol.

Now it is obvious that the enormous quantities of aluminum represented in the table as having been extracted from the soils could not have been completely combined with nitrate, chloride, sulfate and phosphate ions, as the total of these acid ions could account for but a small fraction of the aluminum. It is conceivable that extraction of the soils with potassium nitrate may have converted aluminum combined as aluminum silicates into aluminum nitrate, through replacement of aluminum by potassium, but no such explanation is offered to explain the high quantities of aluminum in the water extract.

TABLE 1

Pounds per acre of aluminum in soil, determined from potassium nitrate and water extracts (2,000,000 pounds to depth of 6⅔ inches)

SOIL	TOTAL ALUMINUM IN ORIGINAL SOIL	ALUMINUM IN POTASSIUM NITRATE EXTRACT	ALUMINUM IN WATER EXTRACTS
	lbs.	*lbs.*	*lbs.*
Gray silt loam	121,000	54,200	21,400
Yellow-gray silt loam	151,200	90,600	33,400
Yellow silt loam	149,400	75,600	32,200

TABLE 2

Soluble alumina in water extracts of soils as reported by Kelley (extraction of air-dry soil)

SOIL NUMBER	ALUMINA	SOIL NUMBER	ALUMINA
	p. p. m.		*p. p. m.*
74	11.1	416	17.6
164	7.5	417	15.3
9	4.8	406	10.3
292	16.6	428	4.4
290	19.1	426	2.9
405	7.6	448	4.9

Finally, in regard to the quantity of soluble aluminum in soils, it is necessary to state that no analyses of water extracts of soils for aluminum that have come to the attention of the writer have revealed more than insignificant quantities of aluminum. Typical of such analyses are the data reported in table 2, which have been reproduced from the work of Kelley (8). These soils, according to Kelley, are acid in reaction although they contain bases. Calculated on the basis of elemental aluminum the results would be one-half of the figures given.

Having established the nature of the compounds in which the soluble aluminum of the soil exists, it would be desirable to throw further light on the conditions surrounding the rise of these compounds in the soil, particularly of the nitrate and sulfate. Several investigators have reported the formation of the

nitrate and sulfate in the soil, namely Abbott, Conner and Smalley (1) Ames and Boltz (2), and Ruprecht and Morse (13). Although it seems probable that these salts exist in very acid soils in quantities sufficient to exert a toxic effect, some doubt exists as to whether the salts were actually present in the quantities reported. At any rate, the soluble hydroxide could have been produced under the conditions of the experiments, and it would have to be eliminated as a factor before the soluble aluminum which is produced in nitrification, sulfofication and by the application of ammonium sulfate could be said to be combined with the particular acid concerned. In other words, the increased acidity that is produced in these processes could readily convert aluminum hydroxide to the hydrosol, but as soon as the acidity of the soil reaches a sufficiently high point, aluminum nitrate and sulfate are certain to be produced.

EXPERIMENTAL

The nature of the problem

It is evident from the foregoing discussion that considerable doubt exists as to the exact form in which soluble aluminum occurs in the soil; whether it occurs principally as salts of the soil acids or whether it is to be found in greater quantity in the form of soluble hydroxide. Until definite information which pointed in one way or the other was obtained, little progress in bacteriological studies could be made. If aluminum salts do not occur in soils in appreciable quantities, then their influence on bacterial activity, while of considerable scientific interest, is hardly of practical value from the standpoint of soil fertility. Consequently, before attempting bacteriological work definite information as to the form in which aluminum salts occur in the soil was sought.

A means of differentiating quantitatively between aluminum as salts and aluminum as the hydroxide was needed. Dialysis at once suggested itself as the most logical means of effecting this result. In respect to the completeness of separation of diffusible aluminum salts from the hydroxide by dialysis, there can be no question, for Jones (6), reviewing the work of Graham on dialysis of aluminum chloride from aluminum hydroxide, states that the aluminum chloride dialyzed without undergoing decomposition and that no trace of chloride was to be found in the alumina after the process had been completed. This statement also removes any doubt as to whether the aluminum salts in passage through the membrane are dissociated into the acid ion and aluminum hydroxide. Furthermore, it is a principle of dialysis that the membrane itself has no influence on the rate of diffusion of molecules sufficiently small to pass through the membrane. Therefore, since aluminum salts diffuse rapidly like any other electrolyte no difficulty should be experienced in effecting complete separation of the salts from the hydroxide. Determination of aluminum after dialysis in the diffused portion and in that portion remaining within the membrane gives at once the quantity of both forms of aluminum in the extract. A method of differentiating the forms of aluminum having been

found, this phase of the problem was reduced to the matter of preparing neutral salt extracts of several acid soils and subjecting them to dialysis.

If aluminum salts are to be found in acid soils, then a complete extracting of the water-soluble acidity of these soils must reveal the presence of aluminum in the extract, since the nitrate, chloride and sulfate of aluminum are easily extractable by water.

Experimental work carried out along the lines that have been suggested should determine the quantity of aluminum as salts of the mineral acids, likely to be found in acid soils. It would then be necessary to ascertain whether the rise of soluble aluminum in the soil is to be ascribed to the replacement of aluminum by other bases or whether it has a biochemical origin or whether both processes may account for its presence. The incubation of aluminum in solution cultures of nitrifying organisms containing no free base but aluminum, and subsequent determination of nitrate and aluminum in the cultures would indicate whether aluminum is rendered soluble in nitrification, or in other words, whether it may serve as the base in nitrification. Likewise incubation of soil with sulfur and dialysis of the extract should show whether soluble aluminum may be formed in sulfofication.

Having determined the quantity of soluble aluminum salts in acid soils, an experiment would be carried out to ascertain whether ammonification and nitrification might be inhibited in such concentrations of salts. Incubation of soil with several concentrations of the aluminun salts likely to be found in the soil should answer this question.

If inhibition of nitrate production should result from the toxicity of aluminum it would be desirable to know what fertilizer material or soil amendment would be most effective in rendering the aluminum inactive.

Description of the soils used

The soils studied in this investigation were the same as those used by Mirasol in his work to which several references have been made. The chemical analyses of these soils as reported by Mirasol are reproduced herewith; quantities are expressed as pounds per acre, assuming that the surface soil to a depth of $6\frac{2}{3}$ inches weighs 2,000,000 pounds, table 3. In addition, a slightly acid brown silt loam from the University South Farm and soil from plot 23 of the Rhode Island Agricultural Experiment Station were used for special studies. The soil of plot 23 has received applications of ammonium sulfate since 1893 and it is extremely acid.

Experiment 1. The nature of the aluminum compounds extracted with potassium nitrate

Using for this experiment the gray, yellow-gray, and yellow silt loams and the Rhode Island soil, an extract of each was made by adding to 100 gm. of soil in a 400 cc. bottle, 250 cc. of a normal potassium nitrate solution, shaking

for 3 hours, and after the supernatant liquid had become perfectly clear, drawing off 125 cc. of the solution for analysis of aluminum. Aluminum was determined in the usual way, by precipitation with ammonium hydroxide. The precipitates were but faintly tinged with the brownish color of ferric hydroxide so that no attempt was made to separate iron from aluminum. As a check upon the results obtained by this procedure, the phenyl hydrazine method for the determination of aluminum was carried out as given by Hillebrand (6). Practically identical results were obtained. Table 4 gives the results of these determinations as the average of triplicate analyses.

TABLE 3

Chemical composition of soils used

CONSTITUENTS	GRAY SILT LOAM	YELLOW-GRAY SILT LOAM	YELLOW SILT LOAM
	lbs. per acre	*lbs. per acre*	*lbs. per acre*
Nitrate nitrogen	26	36	60
Total nitrogen	2,900	1,370	1,966
Phosphorus	1,104	693	691
Potassium	25,130	35,800	29,000
Calcium	4,510	3,920	7,850
Magnesium	4,520	4,180	5,330
Iron	47,800	74,200	74,200
Manganese	840	786	660
Aluminum	121,000	151,000	149,000
Lime requirement	2,125	2,814	2,921

TABLE 4

Aluminum in potassium nitrate extract, after 3 hours' shaking

SOIL	ALUMINUM
	lbs. per acre
Gray silt loam	678
Yellow-gray silt loam	540
Yellow silt loam	366
Rhode Island soil, plot 23	498

These figures, of course, do not represent the total soluble aluminum of the soil since no more can be extracted after equilibrium has been established between the extractant and the soil. Fresh potassium nitrate and renewed shaking would of course bring more aluminum into solution. Aliquots of a second similar series of extracts were than pipetted into 500-cc. collodion flasks for dialysis. These flasks were suspended in separate glass jars containing 3 liters of distilled water and dialysis allowed to take place for 2 days. During each day, water was constantly drawn off and evaporated. Finally, when 1 liter of the diffusate after evaporation to several cubic centimeters

gave no test for nitrate with diphenylamine sulfuric acid, it was assumed that the process of dialysis was complete. The diffusate was evaporated to about 150 cc. heated to boiling and ammonium hydroxide added until the solution was just alkaline. No precipitate whatever of aluminum was obtained. The collodion flasks were then placed in beakers and the collodion disintegrated by digesting with strong nitric acid on a steam bath over night. Determination of aluminum showed that all of the aluminum contained in the extract had been recovered and that none had diffused through the membrane. This result points directly to the fact that all of the aluminum present in the potassium nitrate extract of the soils under study was present as the hydroxide and not as salts. These results completely confirm the work of Knight, who, as was mentioned earlier in this paper, obtained the same results by dialysis of the potassium nitrate extract of an acid soil.

Before concluding definitely that the aluminum which had been found in the potassium nitrate extracts was present as the hydroxide, it was thought desirable to make a study of the hydrosol of aluminum hydroxide, particularly with reference to its appearance, and behavior in the presence of ammonium hydroxide. Some doubt existed at this time as to whether the hydrosol would not appear quite opalescent, whereas the soil extracts were as clear as distilled water. Furthermore, it was not altogether certain that aluminum in the sol state would be precipitable by ammonium hydroxide. In order, then, to remove any doubts as to the appearance and behavior of the sol in so far as this problem is concerned, certain observations were made on aluminum hydroxide in this condition.

Experiment 2. Properties of the hydrosol of aluminum hydroxide

The procedure followed in the preparation of the hydrosol was that of A. Müller, reproduced in Zsigmondy and Spear's Chemistry of Colloids (16). A solution of aluminum chloride containing 1.124 gm. of aluminum oxide in 50 cc. of water was treated wih ammonium hydroxide, washed as quickly as possible with water, and put into 250 cc. of water in a flask. The whole was brought to a boil, and 20 cc. of N/20 hydrochloric acid added drop by drop. The hydrosol prepared in this manner was only faintly opalescent. A portion diluted with water, however, formed a perfectly clear solution. The hydrosol was found to be neutral to both red and blue litmus paper. On addition of ammonium hydroxide with warming, a gelatinous precipitate of aluminum hydroxide was formed. In view of the similarity in appearance and behavior of the aluminum hydroxide hydrosol with that form of aluminum which was found in the potassium nitrate extracts, together with the fact that the aluminum in the extracts failed to diffuse through the collodion membrane, admits of no doubt as to the form in which aluminum was present in the extracts, namely, the hydrosol of aluminum hydroxide.

Experiment 3. Effect of complete extraction of acidity on nature of aluminum compounds in potassium nitrate extracts

The question now arose as to whether, under the conditions of the extraction with consequent production of equilibrium, sufficient aluminum as salts had been extracted to give a determinable amount of aluminum after dialysis, and whether complete extraction of the soil acidity would tend to modify the character of the aluminum compounds extracted. In order then to extract the total amount of soluble aluminum, the soils, except that from Rhode Island, were shaken as before with normal potassium nitrate. After settling, all the supernatant liquid was removed, replaced with fresh salt solution and shaken again. This process was repeated until titration of 125 cc. of the extract required less than 0.5 cc. of standard sodium hydroxide to neutralize it. It was found impossible to go below this figure on account of the slightly acid reaction of the potassium nitrate solution. Six shakings of 3 hours each with replacement of the salt solution after the first five shakings were found to be necessary to reduce the acidity of the last portions to practical neutrality. A similar series was extracted with distilled water, but because two of

TABLE 5

Aluminum in potassium nitrate extract after complete extraction of acidity of soils

SOIL	ALUMINUM
	lbs. per acre
Gray silt loam	1014
Yellow-gray silt loam	765
Yellow silt loam	802

the extracts persisted in remaining turbid, these water extracts were discarded. The results of the analyses for aluminum in the potassium nitrate extracts, appear in table 5.

A comparison of these results with those received from the single shaking with potassium nitrate reveals the fact that from one and one-half to two times as much aluminum is removed by the successive shakings as with a single shaking, which was to be expected. A very striking comparison, however, is made when the second series of results are compared with those obtained by Mirasol (reproduced in table 3), by leaching the same soils to neutrality with normal potassium nitrate. It should be noted in this connection that the procedure followed by Mirasol was quite different from that used by the writer in that the results of the former were obtained from analysis of the soils before and after extraction, no attempt being made to analyze the extract itself. And herein, undoubtedly, lies the reason for the very high results obtained by Mirasol, for it is highly probable that the percolation of the potassium nitrate through the soils carried with it mechanically a very large quantity of finely divided particles of aluminum hydroxide. Naturally

the hydroxide in this form would not be found in analysis of the extract, but it would reduce enormously the quantity of aluminum in the soil after extraction had been completed. This explanation likewise accounts for the large quantity of aluminum which Mirasol found was removed by leaching with water. None whatever could be found in the extract by the writer in repeating the work in exactly the same manner as Mirasol had done, with the exception that the writer made his analysis of the actual extract rather than of the soil itself. Additional support of this result is given by the fact that the bottom of the bottles receiving the percolate was in each instance covered with a noticeable layer of finely divided material, presumably aluminum hydroxide. More detailed consideration of the water extracts will be given later.

The potassium nitrate extracts of the three soils after complete extraction of soil acidity were now subjected to dialysis by concentrating to small volume and dialyzing in the manner previously described. Here another apparently abnormal result was obtained, for all of the aluminum contained in the extract was found to diffuse completely through the membrane and the total quantity of aluminum in the extract was recovered in the diffused portion. Treating the dialyzate with ammonium hydroxide after digestion with acid failed to give a test for aluminum.

Explanation of the presence of aluminum nitrate in the potassium nitrate extract

The fact that with a single shaking of the soils with potassium nitrate only non-dialyzable aluminum was to be found in the extract, while with complete extraction only dialyzable aluminum was found, can be explained only by assuming that the aluminum hydroxide present in the extract after shaking was converted to aluminum nitrate by the increased acidity which resulted from successive shakings over a long period. It might appear possible that the single extract from the shaking contained aluminum as salts in insufficient quantity to be detected, whereas the complete extraction removed a considerably larger amount. This contention, however, is invalidated by the fact that in the first instance non-diffusible aluminum made up the total aluminum content of the extract, whereas in the second instance the total aluminum of the extract consisted of wholly dialyzable aluminum. This fact necessarily presupposes a conversion of aluminum hydroxide to the nitrate and can hardly be explained on another basis.

Assuming such conversion to have taken place, it became necessary to ascertain whether the conversion had occurred as a result of the increased acidity, caused by the repeated shakings, or whether the concentrating of the 800-cc. aliquots to 150 cc. had increased the hydrogen-ion concentration of the solution to a point which would convert the hydroxide to the nitrate. To settle this latter point, dialysis was repeated with larger collodion flasks which obviated the necessity of concentration, but complete dialysis took place as before, thus eliminating the factor of change in the nature of the aluminum compounds due to manipulation.

If the conclusion is accepted that aluminum salts were not present in the extract after the shaking of 3 hours, but that they were produced as a result of contact between the soil and the extract over a much longer period, then certain fundamental considerations must follow. If aluminum salts are not found in the extract after the shorter period of contact then the salts cannot be the real cause of the acidity of the extract. They are produced in side reactions of the true acidic factors within the soil and diminish rather than increase the acidity of the extract to the extent that they fail to hydrolyze completely. The hydrolysis of soluble aluminum salts, on the basis of this reasoning, cannot be a contributing factor to the acidity of the soils under investigation.

A detailed consideration of the probable process by which aluminum nitrate was produced in these soils, follows. The acid soils being deficient in bases, and because of their rather large content of alumino-silicic acids, alumino-silicates, organic acids and of acid salts in general, withdraw the potassium ion from the neutral salt solution until their capacity for base is satisfied. Those compounds containing aluminum then liberate this ion in proportion to the quantity of potassium absorbed. As the potassium ion is withdrawn from the potassium nitrate, hydrogen ions from the various acids and acid salts within the soil combine with the nitrate ion to form nitric acid. The nitric acid thus produced acts upon the aluminum which is replaced by potassium and forms not aluminum nitrate, as would naturally be expected, but forms the hydrosol of aluminum hydroxide. To assume that soluble aluminum hydroxide is produced under these conditions rather than aluminum nitrate probably appears out of harmony with our usual conception of chemical reactions; yet it is necessary to bear in mind the work of Rose on the formation of hydrated aluminum hydrosols in weak acid solution before the acidity is sufficient to form the normal salt. In the soil, undoubtedly, a series of similar hydrated hydrosols are produced until finally the concentration of nitric acid, increasing slowly by the removal of the potassium ion in the rather slow replacement reaction, reaches a point at which aluminum nitrate is produced. It is necessary to point out that contact of the salt solution with the soil over the period of 2 weeks during which the total extractions were made did not result in increased acidity as measured by titration, but in this period the hydrogen-ion concentrations of each of the extracts rose to a point at which the hydroxide was converted to the nitrate. This is to be explained by the fact that hydrogen ions of the weakly dissociated alumino-silicic acids and organic acids which represent the total acidity of these soils, but which affect only slightly the hydrogen-ion concentrations of the soil, were replaced by potassium. The result was the formation of strongly dissociated nitric acid and a consequent increase in the pH value of the extracts. The data reported in table 6 substantiate this contention in that there is seen to be no increase in titratable acidity in soil extracts which have remained in contact with the soils up to 3 months, yet in this interval there has been a singularly large

increase in the concentration of hydrogen ions in the extracts. The results reported in this table were obtained by shaking 100 gm. of soil with 250 cc. of normal po tassium nitrate solution for 3 hours, titrating 125 cc. immediately after settling and also after standing for 1 and for 3 months. Determinations of the hydrogen-ion concentration of the extracts were made by the colorimetric method of Clark and Lubs (4), at the time of the titration.

Examination of the data presented in table 6 reveals some extraordinary changes in the acidity of the soil extracts during the course of the 3 months' standing. The hydrogen-ion concentrations of the extracts have increased considerably by the third month, pointing strongly to the production of a readily ionizable acid, in this case nitric acid. But much more striking are the changes through which the titratable acidity have passed in this period.

TABLE 6

Total titratable acidity and hydrogen-ion concentration of soil extracts after contact with soil for different periods

SOIL	TIME OF CONTACT OF SALT SOLUTION WITH SOIL	TITRATABLE ACIDITY IN TERMS OF STANDARD ALKALI	HYDROGEN-ION CONCENTRATION
		cc.	*pH values*
Yellow silt loam	24 hours	11.0	4.4
Yellow silt loam	1 mo.	3.0	4.2
Yellow silt loam	3 mos.	10.5	2.8
Yellow-gray silt loam	24 hours	9.7	4.0
Yellow-gray silt loam	1 month	9.3	4.0
Yellow-gray silt loam	3 months	9.3	3.0
Gray silt loam	24 hours	4.3	4.6
Gray silt loam	1 month	0.6	4.6
Gray silt loam	3 months	Not determined	Not determined

It will be observed that the total acidity of the yellow and gray silt loams had decreased to a very marked extent after one month's standing but after the entire period had elapsed the total acidity of the former had returned to the original figures obtained by titration after 24 hours. No such change took place in the extract of the yellow gray silt loam; during the whole period, its acidity remained practically constant. Evidently chemical reactions of considerable complexity had taken place in these extracts to account for the fluctuations in the acidity, and no explanation which might be offered without further study might coincide with the actual changes which took place. Nevertheless, a possible explanation might be suggested at this time which would perhaps stimulate further work along this line. It would certainly seem that some of the active hydrogen ions of the extract had been combined into compounds which removed them from the system either through the passage of

the compounds into the colloidal state, e.g., silicic acid, or it may be that compounds were formed containing hydrogen which ionized to only a slight extent. Either of these possibilities would account for the reduction in acidity after one month. Such a reduction in acidity would naturally affect the hydrogen-ion concentration of the extracts. Whereas, the pH value would normally rise immediately with the conversion of the weakly dissociated soil acids to the strongly dissociated nitric acid, it appears from the data presented that the reduction in total acidity, from whatever cause, has prevented the hydrogen-ion concentration from increasing until some time after one month. After this time had elapsed, however, the constantly increasing concentration of nitric acid succeeded in bringing back into the system the acidic compounds which for some reason had been thrown out. It will be observed that the yellow-gray silt loam suffers no change whatever. Evidently it does not contain to an appreciable extent those compounds which by entering the colloidal or insoluble state reduce the acidity of the extract. Whether the explanation that has been suggested is acceptable or not, does not affect the main point, namely, that there was a very considerable reduction in the total acidity of the soils during the early period and subsequent return to the normal acidity of the extracts. Error in manipulation cannot account for the abnormality since a second series of extracts gave similar results with respect to both titratable acidity and hydrogen-ion concentration.

The extracts which had remained in contact with the soil for 3 months were subjected to dialysis with the result that the aluminum compounds in solution in the extracts diffused through the membrane, showing that in the interval of 3 months conversion of aluminum hydroxide to aluminum nitrate had been effected. It should be noted, however, that under the conditions of the extraction, the production of nitric acid is a reversible reaction. Removal of the products of the reaction then would be expected to accelerate its speed. This is exactly what happened in the complete extraction of the soil acidity by repeated shakings with removal of the salt solution after each shaking replacing it with fresh solution. As a result of this procedure, aluminum hydroxide was converted to aluminum nitrate within 2 weeks (the time required for the extraction), whereas even after 1 month's standing without renewal of the salt solution no such change had taken place. The hydrogen-ion concentration of one of the extracts from complete extraction which happened to be saved, corresponded very closely to the pH value of the same soil after 3 months' standing in contact with the salt solution.

In concluding this discussion of the conversion of aluminum hydroxide to the nitrate in the potassium nitrate extracts, it is necessary to emphasize the fact that the hydrolysis of soluble aluminum salts cannot possibly be a factor contributing toward the acidity of soils in general, the term acidity being taken in its true meaning of the effect of free hydrogen ions and not including a toxic effect apart from that of hydrogen ions. Aluminum salts were not found to occur normally in the soils studied but were produced by the interaction of

the soil acids and the potassium nitrate solution. Hence, almunium salts are produced by soil acids and cannot therefore be a cause of the acid reaction of the soil.

Experiment 4. Aluminum in water extracts

Attention has been previously called to the fact that the water extracts of the soils by repeated shakings were too turbid for use in the determination of aluminum. Any attempt to clear the extracts by flocculation of colloidal material, of course, would precipitate aluminum in the hydrosol state. Hence, percolation of the soil with distilled water was resorted to in order to obtain perfectly clear extracts. Five kilograms of each soil was placed in pots of that capacity and leached with distilled water until a 125-cc. portion of the percolate required not more than 0.2 cc. of standard alkali to neutralize it. Approximately 10 liters of water was required by each soil to reduce its acid reaction to neutrality.

Analysis of the water extracts for aluminum was made by evaporating aliquot portions to dryness, allowing the beakers to remain on the steam bath over night to dehydrate the silica, digesting the residue for 1 hour on the bath with 5 cc. of concentrated nitric acid, diluting, and after filtering off the silicia, heating to boiling and treating with ammonium hydroxide in the presence of 2 gm. of ammonium chloride to faint alkalinity. No precipitate whatever formed even when 5-liter aliquots were taken of the total volume of 10 liters of each extract. When it is considered that the total quantity of soil extracted in each case was 5000 gm.; further that there is no reason why any nitrate, sulfate or chloride of aluminum should have failed to be removed by the water had they been present in the soil, the conclusion may be drawn with assurance that soluble aluminum was totally absent from these soils despite the fact that Mirasol has reported between 21,000 and 33,000 pounds of aluminum to have been removed from the same soils by water. The explanation of this discrepancy has been made in connection with the discussion of aluminum in potassium nitrate extract, namely, that these figures reported by Mirasol were not secured by actual analysis of the extracts, but that they represent the loss in total aluminum of the soils after percolation had been accomplished. It was further suggested that the liquid passing through the soil had removed mechanically very fine particles of aluminium hydroxide to which the loss in aluminum may be ascribed. Mirasol, however, does report results from the actual analysis of the water extracts for aluminum. These results are reproduced in table 7.

These results, however, if calculated on the acre basis, vary widely from the results reported by him from analysis of the soils before and after percolation. For instance, selecting the figure given for aluminum in the first 4 liters of the extract of the yellow gray silt loam, namely 105.2 gm. and calculating this in terms of pounds per acre (16 liters of water was the total volume used in leaching the soil), assuming 5000 gm. to be the capacity of the pot used, we

arrive at the figure of 168 pounds per acre; whereas calculation from the results obtained indirectly, i.e., by analysis of the soil before and after percolation, shows that 33,400 pounds per acre had been removed. The figure 168 pounds as a matter of fact is much too large as it is computed from the quantity of aluminum in the first 4 liters which contained considerably more aluminum than the succeeding volumes of water.

It is now necessary to explain the reason for the discrepancy in the results of Mirasol and of the writer in direct analysis of the water extracts. Mirasol does not give his method for the determination of aluminum in the water extracts, so it may be presumed that he disregarded the possible presence of soluble silica in the extracts, treating with ammonium hydroxide to precipitate aluminum directly after evaporation, instead of evaporating the extracts to dryness, dehydrating and removing the silica with subsequent treatment with ammonium hydroxide. It would seem possible then that the precipitate that he obtained with ammonia was not aluminum hydroxide but silicon hydroxide. In order to obtain experimental evidence bearing on this point, the writer evaporated 4 liters of each of the extracts to 200 cc. and treated with

TABLE 7

Analysis of water extracts as reported by Mirasol

SOIL	ALUMINUM
	mgm.
Yellow silt	88.9
Yellow-gray silt loam	105.2
Gray silt loam	75.5

ammonium hydroxide, white gelatinous precipitates being formed in each case. One of the precipitates was pure white, the others were tinged somewhat by ferric hydroxide. Boiling these precipitates with strong sodium hydroxide failed to dissolve them. Even boiling with fairly strong acid brought them into solution only quite slowly. The behavior of these precipitates with acid and alkali should remove any doubt that they were not aluminum hydroxide.

Resuming further consideration of Mirasol's data concerning the presence of aluminum in water extract, it is necessary to say first that it is utterly impossible that all of the aluminum which Mirasol succeeded in extracting from the soil by water was present as salts of the various acids. By calculation of the amount of aluminum that would be combined with the total quantity of negative ion in the extract, assuming for the time that all of the acid ions are present as aluminum salts, it is possible to approximate the maximum quantity of aluminum that might be contained in the extract as salts. This figure compared with the total quantity of aluminum present gives the ratio of aluminum as salts to the total aluminum content. This idea has been carried out with results that appear in table 8. All of the data with the

exception of the analysis of chloride and sulfate, which were carried out by the writer, are taken from Mirasol's report of his work.

A comparison of the maximum amount of aluminum which could be combined with the total quantity of acid ions, leaving the silicate out of consideration, demonstrates at once the extremely small proportion of aluminum that could be present as salts. But we know from the principles of water analysis that the acid ions are not linked with aluminum but with calcium, magnesium, potassium and sodium. All bases, in excess, are assumed to be present as hydroxides.

In no case in water analysis, to the knowledge of the writer, are acid ions, under normal conditions, ever assigned to aluminum. The only alternative to account for the large amounts of aluminum is to ascribe it to the presence of aluminum hydroxide. The writer, of course, does not lose sight of the fact that aluminum hydroxide will be generally admitted to be present in the

TABLE 8

Acid ions in soil solutions extracted by water, with their aluminum equivalent

IONS	GRAY SILT		YELLOW-GRAY SILT		YELLOW SILT	
	Acid ions	Aluminum equivalent	Acid ions	Aluminum equivalent	Acid ions	Aluminum equivalent
	lbs. per acre	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*
Nitrate	18	3	26	4	62	9
Chloride	152	38	212	53	112	28
Sulfate	422	79	598	112	459	86
Phosphate	*	*	*	*	13	3
Total		120		169		126
Total aluminum estimated	21,400 lbs.		33,400 lbs.		32,200 lbs.	

* Amount within error.

water extract of soils; Mirasol, in fact, mentions its probable occurrence in the soil solution. The writer also recognizes the possibility of its presence being a potential source of toxic aluminum, but he does not admit the correctness of grouping it with aluminum in the form of salts under the head of active aluminum, i.e., aluminum that is toxic to plants. It follows, therefore, that the total aluminum which may be found in water extracts cannot be taken as a measure of toxic aluminum since the latter occurs to the best of our knowledge only as salts which, as has been shown, are not likely to be present in soils in significant amounts.

THE PRODUCTION OF SOLUBLE ALUMINUM IN THE SOIL BY BACTERIAL ACTIVITY

Thus far in this paper no data have been adduced which indicate that the rise of aluminum salts within the soil might contribute towards its acidity. It has been shown that aluminum salts produced by purely chemical reactions

cannot possibly augment the acid reaction of the soil. It is now necessary to consider whether soil acidity might be increased by the hydrolysis of aluminum salts produced biochemically, namely, by nitrification and by sulfofication. Mirasol has emphasized the former process as being the foremost factor in the production of soluble aluminum, pointing out that in absence of a more suitable base, aluminum may serve as the base in nitrification with the production of considerable quantities of aluminum nitrate. That this process may take place to any extent, however, may be doubted in view of the fact that nitrifying bacteria are extremely sensitive to an acid medium which would rapidly be brought about by the hydrolysis of aluminum nitrate, if formed. Certainly nitrification could not go on appreciably under such conditions. Nevertheless, it was deemed desirable to study this question experimentally.

Experiment 5. Nitrification as a factor in the production of soluble aluminum

This experiment was performed by determining the amount of nitrate in incubated nutrient media which contained no free base which might neutralize nitric acid except aluminum hydroxide and aluminum phosphate.

TABLE 9

Nitrate production in liquid cultures

TREATMENT OF NUTRIENT MEDIUM BEFORE INOCULATION WITH SOIL INFUSION	NITRATE NITROGEN	
	After 4 weeks	After 6 weeks
	mgm.	*mgm.*
$(NH_4)_2SO_4$	1.1	1.0
$(NH_4)_2SO_4$ and $Al(OH)_3$	0.6	0.9
$(NH_4)_2SO_4$ and $AlPO_4$	0.5	0.5
$(NH_4)_2SO_4$ and $CaCO_3$	5.5	5.3

The nutrient medium contained per liter of distilled water, 1 gm. of K_2HPO_4, 0.2 gm. of $MgSO_4$, 1 drop of 10 per cent $FeCl_3$, 1 gm. of NaCl and a very small amount of $CaCl_2$. Twenty-five cubic centimeters of the medium was poured into 500 cc. Erlenmeyer flasks, each of which received in addition sufficient standard $(NH_4)_2SO_4$ solution to provide 10 gm. of nitrogen. Aluminum hydroxide and phosphate were added to separate series of flasks in amounts sufficient to neutralize all of the nitric and sulfuric acids that might be produced, plus a slight excess. The flasks were then inoculated with 1 cc. of a soil infusion made by shaking 100 gm. of a black clay loam soil with 200 cc. of water and allowing the supernatant liquid to stand until most of the soil particles had settled. Incubation at 30° was allowed to continue for 4 and for 6 weeks. At the end of these intervals, the contents of the flasks were analyzed for nitrate with results as given in table 9 as averages of triplicates.

From the data contained in the table there does not seem to be any likelihood of aluminum replacing calcium as an available base in nitrification. The experiment, however, probably does not admit of a definite conclusion on this point, since it might be that in a much longer period of incubation the aluminum compounds would slowly be attacked and a measurable quantity of nitrate would be formed. In addition, there is a possibility that if nitrification were intiated by a slight amount of carbonate, aluminum would carry on the process.

Experiment 6. The production of soluble aluminum in the soil by the process of sulfofication

It will be recalled that reference was made earlier in this paper to the fact that Ames and Boltz (2) report aluminum as having been rendered soluble in the process of sulfofication. As their experimental procedure did not discriminate between the two forms in which aluminum may be produced in the soil, i.e., as the hydroxide or as salts, it became necessary in order to study this problem to induce strong sulfofication in a soil and then to dialyze the extract as in the previous experiments. Accordingly, 100-gm. portions of the yellow gray soil were placed in tumblers, 0.5 gm. of sulfur was added, 0.8 gm. of dried blood, and finally enough precipitated aluminum hydroxide to double the aluminum content of the soil. Water was then added to optimum moisture content and the tumblers incubated at room temperature for 2 months, water being added from time to time to keep the tumblers at a fixed weight. At the end of the incubation period the contents of each tumbler were transferred to a 400-cc. shaker bottle, 200 cc. of distilled water added and the mixture shaken for 1 hour. After the suspended material had settled aliquot portions were drawn from each bottle, sulfate being determined from two portions, the remainder being dialyzed in the manner that has been previously described. Very strong oxidation of sulfur was found to have taken place, the sulfuric acid formed being sufficient to increase the pH value of the soil extracts from 4 to 3. Under such conditions, it was not surprising that conversion of aluminum hydroxide to sulfate took place as was demonstrated by dialysis. It is hardly necessary to point out that the aluminum sulfate formed in this manner could not possibly have been a factor in increasing the acidity of the soil extracts since this was of course due solely to the sulfuric acid formed.

Experiment 7. The influence of aluminum salts on ammonification and nitrification

Although thus far in the experimental work that has been reported in this paper, no evidence has been adduced that has indicated the presence of aluminum salts in acid soils under normal conditions; yet we are confronted with the results of the work of Hartwell and Pember (11), which seems to admit of no other conclusions than that aluminum was the toxic factor which account-

ed for the unique difference in the response of rye and barley to identical soil conditions. Other work which hardly need be reviewed at this time points quite clearly to the harmful influence of those salts in acid soils. Acid soils under a given set of conditions, as in sulfofication, may favor the production of aluminum salts; and, because of their very high toxicity, plant growth might be seriously affected, even though the absolute quantity of salts produced at any one time may be very small.

With these considerations in mind and in view of the lack of data in the literature bearing on the influence of aluminum salts on ammonifying and nitrifying organisms, it was deemed advisable to study to what extent the soil flora concerned in nitrate production reacts toward toxic aluminum. Data which would demonstrate the relative toxicity of the aluminum salts likely to occur in the soil, also seemed of sufficient importance to warrant some attention being given to this phase of the subject. Furthermore, if aluminum was found to inhibit seriously the normal functioning of the nitrifying organisms, it would be of considerable practical importance to ascertain the relative value of certain common fertilizing materials for inactivating the toxic aluminum. A description of the experiments devised to throw light on these points follows.

The soil selected for this work was a slightly acid brown silt loam from the University South Farm. Its lime requirement according to the Hopkins method was 300 pounds per acre. It had a high ammonifying and nitrifying power and for this reason was more suitable than any of the acid soils used in connection with the work on extraction of aluminum. An obvious objection to the use of a soil with such a slight degree of acidity is that aluminum applied to it in the form of salts would be precipitated until the acidity of the salts had increased the hydrogen-ion concentration of the soil beyond the point at which aluminum is thrown out of solution. It was planned, however, to apply the aluminum salts over so wide a range of concentrations that no difficulty would be experienced in bringing about, for the duration of the experiment at least, the presence of soluble aluminum in the soil. Time did not permit a complete chemical analysis of the soil, but for the sake of information an analysis is presented in table 10 which represents the average chemical composition of the soil of the same type in the county from which the sample was taken. These data were obtained from the Soil Report of Champaign County, Illinois and was prepared by the University of Illinois.

One-hundred-gram portions of the soil were placed in tumblers and mixed with organic matter consisting of a mixture of alfalfa and sweet clover residues and furnishing the nitrogen equivalent of 200 pounds per acre. The nitrate, chloride, sulfate and phosphate of aluminum were then applied to separate series in chemically equivalent amounts. The concentrations of salts are indicated in table 11. With the exception of the phosphate, all of the salts were added in solution. Water was added in amounts such that the total volume of liquid applied, that is water and the aluminum salt solution,

was 25 cc., the optimum moisture content of the soil. This moisture content was maintained as nearly as possible during the incubation period by adding from time to time the amount of water lost from several weighed tumblers.

TABLE 10

Composition of brown silt loam of Champaign County

COSTITUENT	AVERAGE AMOUNT FOUND PER ACRE OF TWO MILLION POUNDS
	lbs.
Total nitrogen	4,670
Total phosphorus	1,060
Total potassium	35,430
Total magnesium	9,550
Total calcium	10,680

TABLE 11

Concentrations of aluminum salts used and field rates of application

CONCENTRATION NUMBER	FRACTION OF MOLECULAR WEIGHT PER 100 GM. SOIL	$Al(NO_3)_3$	$AlCl_3$	$Al_2(SO_4)_3$	$AlPO_4$
		lbs. per acre	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*
1	156×10^{-7}	67	42	107	38
2	625×10^{-7}	266	167	427	153
3	25×10^{-5}	1,064	669	1,709	610
4	1×10^{-3}	4,255	2,688	6,836	2,440
5	4×10^{-3}	17,019	10,670	7,348	9,759

TABLE 12

Ammonia production in soil treated with aluminum salts after incubation, per acre in pounds

CONCENTRATION NUMBER	$Al(NO_3)_3$		$AlCl_3$		$Al_2(SO_4)_3$		$AlPO_4$	
	1 week	2 weeks	1 week	2 weeks	1 week	2 weeks	1 week	2 weeks
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
Check	24	23	24	23	24	23	4	23
1	29	16	29	20	36	26	34	28
2	27	16	30	16	32	24	30	24
3	40	18	30	19	32	21	28	16
4	36	20	39	58	26	12	32	24
5	33	34	40	36	21	0	50	23

The experiment consisted of four series, namely ammonia production in 1 week and in 2 weeks, and nitrate production in 1 and in 2 months of incubation. The results as reported in tables 12, 13 and 14 are averages of the analyses of duplicate tumblers. Whenever difficulty was met in obtaining

satisfactory checks that section of the work was repeated. Ammonia was determined by distilling with magnesium oxide, nitrate by boiling off ammonia with sodium peroxide and distilling with Devarda alloy.

TABLE 13

Nitrate production in soil treated with aluminum salts, after 1 month's incubation

NUMBER	NITRATE FOUND AFTER TREATMENTS INDICATED					
	$Al(NO_3)_3$			$AlCl_3$	$Al_2(SO_4)_3$	$AlPO_4$
	Total found	Applied as $Al(NO_3)_3$	Found in excess of that applied.			
	lbs. per acre	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*
Check	126		126	126	126	126
1	185	12	173	33	141	90
2	84	48	36	33	111	135
3	174	192		96	90	135
4	173	768		48	72	174
5	159	2,072		54	174	204

TABLE 14

Nitrate production in soil treated with aluminum salts, after 2 months' incubation

NUMBER	NITRATE FOUND AFTER TREATMENTS INDICATED					
	$Al(NO_3)_3$			$AlCl_3$	$Al_2(SO_4)_3$	$AlPO_4$
	Total found	Applied as $Al(NO_3)_3$	Recovered			
	lbs. per acre	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*
Check	54		54	54	54	54
1	82	12	72	72	110	90
2	90	48	42	66	99	60
3	114	192		72	62	48
4	201	768		72	93	78
5	336	3,072		60	76	Lost

Discussion of results from ammonification and nitrification

Considering first the ammonia determinations after 1 week's incubation, we may say that no toxic effect is to be noted; as a matter of fact, a considerable stimulation seems to be the rule even in the very high concentrations. No great depression of ammonia takes place after 2 weeks except in the highest two concentrations of aluminum sulfate and in a few other cases. These variations may be explained by the fact that nitrate production was stimulated at these particular concentrations, a fact which is borne out in part by the nitrate data.

Turning now to the data of nitrate production after 1 month we find as might have been predicted from our knowledge of the sensitivity of the nitrate and nitrate organisms to acidity that, with the exception of the phosphate in which there is stimulation, there is a general decrease in nitrate formed with increasing concentrations of the salt. The high result in the fifth concentration of aluminum sulfate is to be explained by a disturbance in the system brought about by the high acidity. No doubt the aluminum has exerted its toxic effect as in the other concentrations, but this effect is masked by the dissolving out of some elements to which the bacteria readily responded. The results from the applications of aluminum nitrate are altogether unsatisfactory because none of the nitrate applied in the higher concentrations could be recovered after incubation. Apparently the conditions were favorable for the rapid development of a nitrate consuming flora, or denitrification may have taken place. It was predicted that the phosphate would probably not exert a toxic effect, and it was incorporated in the series partly with the idea in mind of finding whether the nitrifying bacteria would respond to quite insoluble phosphate. Then, it was reasoned, if the phosphate ion is removed by the organisms, the free aluminum ion may have opportunity to exert a toxic effect by combining with an acid radical. The phosphate, it would seem, is quite available to bacteria.

The nitrate results after 2 months' incubation are quite striking in that they demonstrate the fact that soluble aluminum is slowly precipitated or thrown out of action in some way by the soil even in the very highest concentrations. It is realized, as has been indicated before, that a soil of this character would likely dispose of considerable active aluminum by precipitation, and for this reason the objection might be raised that the results are not applicable to normally acid soils. Yet, if this soil is able to dispose of some 27,000 pounds of aluminum sulfate and 10,000 pounds of aluminum chloride, it would seem that a more acid soil could inactivate the much smaller quantities of aluminum salts that it is likely to contain.

For some unknown reason the magnitude of the results from the 2 month's incubation is lower than that from the incubation of a single month. Possibly denitrification resulted from an excess of water that might have been added during the course of the incubation period, or it may be that after the maximum quantity of nitrate had been produced a considerable quantity of nitrate was utilized by a strong nitrate consuming flora. The general trend of the data, however, is not affected by the rather low production of nitrate in the longer incubation period.

Experiment 8. The influence of fertilizing material on the precipitation of aluminum

The final experiment to be reported has to do with the relative efficiency of certain fertilizer materials, namely calcium carbonate, monocalcium phosphate and tricalcium phosphate in diminishing the toxicity of aluminum.

Each of these compounds was mixed with soil in the amounts necessary to precipitate the aluminum from aluminum chloride which was added to the soil in the same concentrations that were employed in the previous experiments. The precipitation of the aluminum from aluminum chloride was assumed to take place according to the following equations:

$$2\ AlCl_3 + 3\ CaCO_3 = 2\ Al_2O_3 + 3\ CaCl_2 + 3\ CO_2$$
$$2\ AlCl_3 + 3\ CaH_4(PO_4)_2 = 2\ AlPO_4 + 4\ H_3PO_4 + 3\ CaCl_2$$
$$2\ AlCl_3 + Ca_3(PO_4)_2 = 2\ AlPO_4 + 3\ CaCl_2$$

Incubation was allowed to take place for 1 month. The results with tricalcium phosphate were unsatisfactory, so a second series was incubated.

TABLE 15

Effect of carbonate and phosphates in inactivating soluble aluminum as measured by nitrate production

CONCENTRATION NUMBER	$AlCl_3$	$AlCl_3 + CaCO_3$	$AlCl_3 + CaH_4(PO_4)_2$
	lbs. per acre	*lbs. per acre*	*lbs. per acre*
Check	126	126	126
1	63	186	78
2	63	183	108
3	96	153	102
4	48	172	84
5	54	87	36

TABLE 16

Effect of tricalcium phosphate in inactivating soluble aluminum as measured by nitrate production

CONCENTRATION NUMBER	$AlCl_3$ ALONE	$AlCl_3 + Ca_3(PO_4)_2$
	lbs. per acre	*lbs. per acre*
Check	120	120
1	108	126
2	93	105
3	66	92
4	105	99
5	75	30

The results from this second series with tricalcium phosphate should be compared with the results from the aluminum chloride series which accompanied it, rather than with the results of the first series. Chemically pure chemicals were used.

The superiority of calcium carbonate over the two phosphates precipitating aluminum as measured by nitrate production is apparent at once. The monocalcium phosphate is likewise to be preferred to the tricalcium phosphate for this purpose.

SUMMARY

The experimental work that has been reported, together with the interpretations of which it admits, have established conclusively the fact that aluminum salts were not present in the acid soils which were used in this investigation. Although aluminum nitrate was found in the potassium nitrate extract of the soils after complete extraction of the acidity had been accomplished, this fact by no means establishes the normal occurrence of aluminum salts in these soils. The very fact that not a trace of soluble aluminum was found in the water extracts is conclusive evidence of its absence, as there is no reason why salts of aluminum, if present, should not have been extracted by distilled water. It has been shown further that even if the total content of acid ions within the soil were combined with aluminum, even this impossible condition could account for only an insignificant quantity of total aluminum extracted.

Soluble aluminum salts may be produced from aluminum hydroxide in acid soils by the action of the mineral acids formed by removal of the basic ion of sulfates, chlorides and nitrates. The basic ions replace aluminum in certain soil minerals, the aluminum coming into solution as the hydroxide. With increasing hydrogen-ion concentration of the soil solution, brought about by the production of highly ionized acids by withdrawal of the bases from salts, a point is reached when aluminum hydroxide in solution is converted into soluble aluminum salts. Since the hydrolysis of these salts cannot increase the acidity of the soil beyond the degree of acidity existing at the time of their formation, the conclusion may be definitely drawn that aluminum salts are not a factor in the acidity of soils, taking the term acidity to refer to the effect of free hydrogen ions and not including a toxic effect due to other causes. Rather than causing an acid condition in soils, aluminum salts are themselves produced by the acidity of the soil, and hence cannot contribute toward it.

It has been shown that the presence of soluble aluminum salts stimulates ammonification while nitrification proper is affected adversely with increasing concentration of the salts. This inhibitive effect, however, is obtained in the soil used only for a relatively short time, perhaps no longer than a month. After 2 month's incubation it is striking to note that, with nitrate production as the criterion, the soluble aluminum had been rendered inactive. Calcium carbonate was shown to be more effective than either monocalcium or tricalcium phosphate in precipitating aluminum, as measured by nitrate production.

CONCLUSIONS

1. Soluble aluminum salts were not present in the acid soils used in this investigation.

2. Aluminum salts, although perhaps occurring in some acid soils, do not contribute to their total acidity, but are themselves produced by the action of the soil acids.

3. Aluminum salts are stimulating to ammonifying organisms, but act adversely upon nitrate bacteria in soil. This effect, however, is temporary only, as an acid soil seems to have considerable capacity for inactivating toxic aluminum.

4. Calcium carbonate is the most effective material, in reducing the toxic action of aluminum salts on nitrification.

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STUDIES OF SULFUR OXIDATION IN SULFUR-FLOATS-SOIL MIXTURES[1]

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EFFECT OF AERATION

The process of mixing rock phosphate, sulfur and soil according to the Lipman formula for the purpose of converting the insoluble into soluble phosphates, is based upon the phenomenon of the oxidation of sulfur by microörganisms. The sulfuric acid produced reacts with the tricalcium phosphate forming the secondary and primary salts. These are soluble in water and in neutral ammonium citrate and thereby readily available for plant use. This process may be expressed in terms of chemical reactions and studied from an empirical standpoint. The equations are:

$$2S + 2H_2O + 3O_2 = 2H_2SO_4$$
$$Ca_3(PO_4)_2 + H_2SO_4 + 2H_2O = Ca_2H_2(PO_4)_2 + CaSO_4 \cdot 2H_2O$$
$$Ca_2H_2(PO_4)_2 + H_2SO_4 = CaH_4(PO_4)_2 + CaSO_4$$

Examining the first equation the outstanding feature is the consumption of large amounts of oxygen in the process of oxidation of sulfur. It is, therefore, suggestive to assume that the microörganisms concerned in the process are strictly aerobic and responsive to a higher oxygen tension. Both of these questions have been the subject of study of Lipman and McLean (8, 9). The aerobic nature of the microörganisms in question has been definitely established. The oxygen tension has also been studied but not to any great extent and the limits of oxygen supply have not been established. It was with this in mind that the following work was conducted.

Mixtures of 50 gm. of floats, 25 gm. of flowers of sulfur and 25 gm. of dry soil were made, moistened to within 50 per cent of the total water-holding capacity, and placed in 250 cc. wide-mouth bottles. Each bottle with the mixture was inoculated with a 5-cc. infusion made by mixing 10 gm. of floats-sulfur-soil compost known for its efficacious oxidizing power with 50 cc. of water.

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[2] The author wishes to acknowledge his appreciation of the enthusiasm and guidance of Dr. Jacob G. Lipman.

Nine bottles, each containing this same mixture, were arranged in series and aerated as shown in figure 1. *A* represents a flask with ordinary tap water. *B* is the first bottle containing the mixture, *C* the second, etc. Air enters bottle *A*, through tube *T*, passes through the water, becomes somewhat saturated and passes to bottle *B*. Tube *D* has at its lower end, a bulb, *b*, $\frac{3}{4}$ inch in diameter. The stream of air enters the mixture through a dozen or more pin holes in this bulb, passes through the mixture and leaves the bottle *B* through tube *E* to enter bottle *C* and repeat the operation. The essentials of this aeration apparatus have been taken from Folin's (4) aeration apparatus for the determination of ammonia. Suction was accomplished by an apparatus used at this station and described by Neller (10).

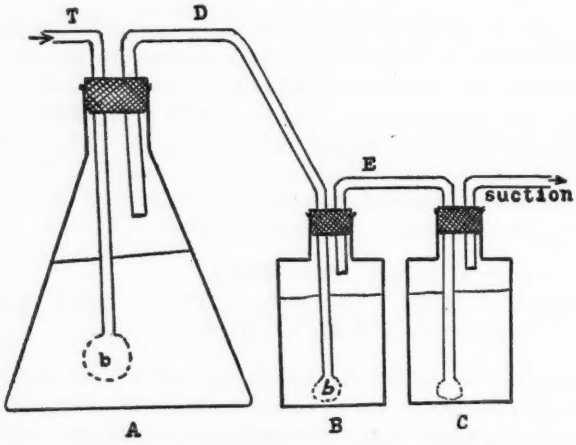

FIG. 1. DIAGRAM SHOWING METHOD OF AERATION

Two bottles served as controls which were, therefore, not aerated. Each bottle throughout the aeration experiment was weighed weekly, water was added to make up for loss through evaporation and also for water taken up in the oxidation of sulfur as shown in the equation:

$$2S + 2H_2O + 3O_2 = 2H_2SO_4$$

It was found that the aerated bottles near the water bottle *A*, lost more water than those at the end of the system near the suction connection. This made it necessary to change the order of the bottles two or three times a week in order to give all the bottles a fairly even chance and thus eliminate a variable. Besides the moisture factor, the question of amount of oxygen was involved in the changing of the bottles from one end of the system to the other. As the air proceeds toward the last bottle, the oxygen in it is used up by the microörganisms. The greater the distance from the source of air, therefore, the less is the amount of oxygen supplied to the microörganisms. It is hoped in

future work, to measure the incoming and outgoing oxygen and thus determine the oxygen requirements of the sulfur-oxidizing organisms. From time to time, the bottles were sampled for determination of hydrogen-ion concentration and phosphorus soluble in neutral ammonium citrate. The colorimetric method as described by Clark (3) was used for the pH determinations and the official method (11) for the phosphorus determinations. The results of the experiment are shown in table 1.

A glance at the figures in table 1, shows that there was, after 100 days, 6 per cent more of the citrate-soluble phosphorus, in the aerated mixtures than in the non-aerated mixtures. After that time the aeration had no effect and the difference between the two series remained about the same.

TABLE 1

Comparison of aerated and non-aerated sulfur-floats-soil mixtures

AGE OF CULTURES	AERATED SAMPLES*		NON-AERATED SAMPLES†		EXCESS OF PHOSPHORUS MADE AVAILABLE BY AERATED MIXTURE OVER NON-AERATED
	Acidity	Phosphorus made available	Acidity	Phosphorus made available	
days	*pH*	*per cent*	*pH*	*per cent*	*per cent*
0	6.4	7.5	6.4	7.5	0.0
10	4.2	12.5	4.8	9.6	2.9
25	4.0	19.6	4.2	15.0	4.6
80	2.8	33.2	2.8	28.8	4.4
100	2.6	36.3	2.8	30.0	6.3
120	2.6	39.8	2.8	33.9	5.9
130	2.6	41.7	2.6	35.7	6.0
150	2.6	46.8	2.6	41.0	5.8
180	2.4	49.9	2.6	44.4	5.5

* Samples, taken in duplicate, were representative of the material in the entire series of nine bottles.

† Samples representative of material in both control bottles.

The same phenomenon was observed in the reaction. In analyzing the sulfur oxidation equations from a physico-chemical viewpoint, it must be remembered that the velocity of a reaction is proportional to the product of the active masses of substances involved. In this case, the active masses of oxygen has been increased through aeration and, of course, there should be an increase in oxidation. There are, however, other factors beside mass that enter a reaction of this nature. It must be remembered that the microörganisms must come in contact with the sulfur in order to oxidize it and that they have need of great masses of oxygen. Thus, the increased oxygen supply is of direct benefit to the microörganisms. It is known that the food supply in any medium brings forth competition among the different groups of microörganisms. Any condition that will favor a certain group of organisms will place this group in an advantageous position at the expense of the others. In the case of non-aeration, the oxygen supply in the beginning was used up by

the different groups, outside the sulfur bacteria, and the sulfur-oxidizing organisms were deprived of their required oxygen. This will explain also why after the reaction reached a certain point, no advantage has been derived from aeration. In the beginning, many other species of organisms were present in the mixtures as shown by the plate method. But when the reaction went

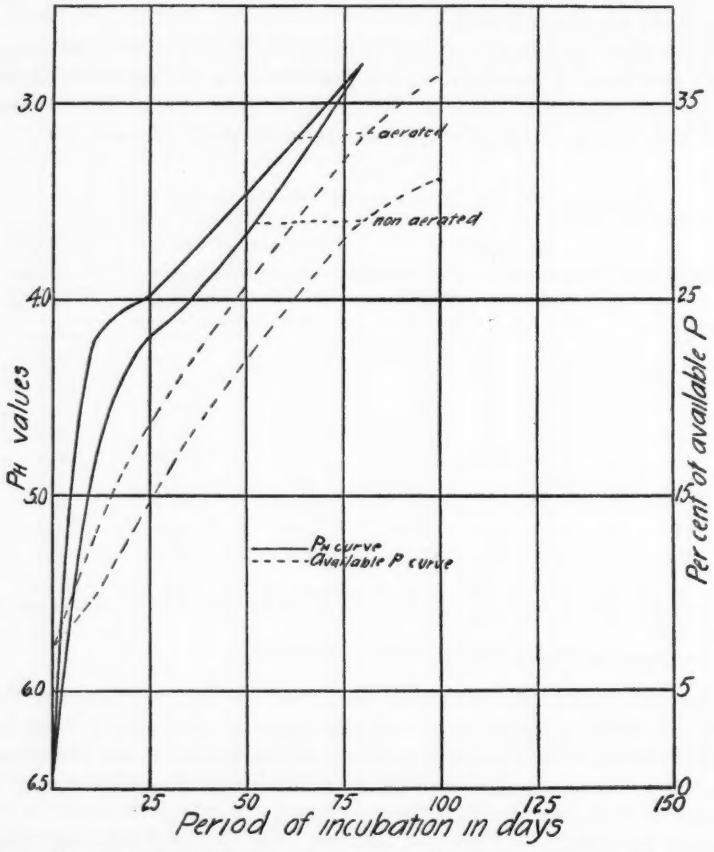

FIG. 2. CURVES SHOWING RELATION OF AERATED AND NON-AERATED CULTURES EXPRESSED BY THE PER CENT OF AVAILABLE PHOSPHORUS AND REACTION

down to a pH 2.8 no bacteria appeared on the plates; as a matter of fact no organisms, except a fusarium, were present. Microscopic examinations showed the typical minute rod-shaped bacteria with rounded ends. Thus the sphere of action at a pH 2.8–2.6 is left to the sulfur-oxidizing bacteria only.

Until the pH of the non-aerated mixtures reached the value 2.8, their bacteria were the least active, as seen from the table 1. As soon, however, as

the reaction was reduced to a pH 2.8, these non-aerated mixtures produced soluble phosphates as fast as the others. The normal supply of oxygen as found in the atmosphere seems to be sufficient at the particular reaction under the conditions of the experiment. Thus the limits of oxygen tension must be taken into consideration. In composting rock phosphate and sulfur, depth of layer is of prime importance, from the standpoint of oxygen supply especially until the reaction goes down to a pH 2.8. It may be deduced from what has been said about the relation of aeration to reaction that it is essential in the composting process to impart to the surrounding medium a reaction as expressed by a pH value of 2.8. That this is not so will be pointed out later in discussing the question of the effect of reaction on the speeding up of the process of sulfur oxidation.

While weighing the bottles to measure the loss of water by evaporation, it was noted that after 80 to 100 days the mixtures gained in weight instead of losing, even though they dried up. The reason for this was not clear at first but the writing out of the equation representing the reaction solved the difficulty.

$$2\ S + 2\ H_2O + 3\ O_2 = 2\ H_2SO_4 + 282\ Cal.$$

Thus two atoms of sulfur need two molecules of water and three molecules of oxygen to make up two molecules of sulfuric acid. The water serves a double purpose, that of supplying water for the sulfuric acid formed and that of keeping the mixtures at an optimum moisture condition for the development of the organisms. The gain in weight may be calculated from the equation:

$$2\ S + 3\ O_2 + 2\ H_2O = 2\ H_2SO_4$$
$$64 + 48 + 36 = 196.$$

Thus for sixty-four units of sulfur we get one hundred ninety-six units of sulfuric acid, or for every gram of sulfur we get 3.02 gm. of sulfuric acid, a gain in weight of more than 2 gm. for every gram of sulfur oxidized. This makes the moisture problem in the composting of sulfur and floats more complicated, since at any moment of the reaction, the increment of sulfuric acid produced determines the moisture content. The moisture content becomes a function of the sulfur oxidized. In order to determine accurately the loss of moisture, a determination has to be made, but this is a tedious method and a more simple one may be used. It consists in determining the total sulfates by the 1 per cent HCl method described by Brown and Kellog (2) and calculating the amount of sulfur oxidized. The equation of sulfur oxidation may be then used for the calculation of water of constitution of the sulfuric acid formed. The amount of water lost by evaporation may be determined by keeping a control with the same mixture, leaving out the sulfur, and substituting sand for it.

Loss of weight by the control will give the moisture lost by evaporation. One other point must be considered in a theoretical consideration of water con-

sumed in the process of sulfur oxidation, namely, the water of crystallization of the gypsum formed in the reaction of the sulfuric acid on the ground rock phosphate. Two molecules of water are tied up with one molecule of calcium sulfate. The latter may also be calculated from the equations given previously.

INFLUENCE OF INITIAL REACTION

It has been pointed out that aeration ceased to be a factor in the mechanism of sulfur oxidation after the mixtures reached a pH value of 2.8.

In an earlier paper, Lipman and Joffe (7) have reported the results of an experiment planned to study the influence of the initial reaction on the oxidation of sulfur. They concluded that under the conditions of their experiment there is no advantage in starting with a relatively high hydrogen-ion concentration through conditions of sulfuric acid. To see the effect of reaction on the oxidation of sulfur in mixtures as in the aeration experiment was the primary object of the experiment recorded. The experiment reported here was carried out under entirely different conditions.

PROCEDURE

Mixtures were prepared in the same way as for the aeration experiment. Tumblers were used instead of bottles. They were kept at room temperature and acidified as indicated in table 2.

Each tumbler received 20 cc. of water and 5 cc. of infusion as in the aeration experiment. The pH determinations were made several hours after the addition of the acid.

The addition of the acid did not bring the reaction down to a pH 2.8. This can be explained by the composition of the mixture. Fifty per cent of it was rock phosphate, which easily removed the hydrogen ions from the sphere of reaction. The twenty-five grams of soil undoubtedly absorbed or adsorbed most of the acid, withstanding the "attacks" of the hydrogen ions through the buffers present in the soil. Still the total acidity increased and exerted some influence. Table 3 records the developed reaction and the availability of the phosphates for a period of four months. It brings out some interesting features of the effect of reaction on the oxidation of sulfur.

The results are not striking and not absolutely conclusive. The indications, however, are interesting. It seems that small additions of sulfuric acid have a beneficial effect on the process of sulfur oxidation in sulfur-floats-soil composts. The first three cultures through the whole period of incubation showed consistently more activity than the remainder. The reaction and also the percentage of soluble phosphates are the expressions of these activities. The control mixtures were favored by conditions fully as much as those treated with larger amount of acids, perhaps even a little more, if the chemical effect of the initial addition of sulfuric acid to the others is considered. Of course, differences are due to the additions of sulfuric acid, but how and why remains

TABLE 2

Treatment of sulphur-floats-soil mixtures

NUMBER OF TUMBLER	AMOUNT OF CONCENTRATED H_2SO_4 SPECIFIC GRAVITY 1.81 ADDED	pH AFTER TREATMENT
	cc.	
1*	0.125	6.4
2	0.250	6.3
3	0.375	6.2
4	0.500	6.2
5	0.625	6.0
6	1.250	5.0
7	0.000	6.4

* All treatments were in triplicate, and, with few exceptions, all results are averages of these.

TABLE 3

Sulfur oxidation as indicated by reaction and availability of phosphate after various periods of incubation

NUMBER OF CULTURE	7 DAYS		18 DAYS		27 DAYS		37 DAYS		44 DAYS	
	pH	Available P	pH	Available P	pH	Available P	pH	Available P	pH	Available P
		per cent		*per cent*		*per cent*		*per cent*		*per cent*
1	5.1	4.5	3.8	5.0	3.8	5.2	3.4	6.4	3.2	7.5
2	5.0	4.8	3.8	5.1	3.8	5.32	3.0	5.9	3.2	8.7
3	4.8	4.6	3.6	5.1	3.6	5.48	3.4	6.3	3.2	7.4
4	5.2	4.5	3.8	5.15	3.8	5.26	3.8	...	3.8	7.4
5	5.4	4.8	4.8	5.1	4.6	4.81	3.9	5.0	4.1	5.48
6	4.6	4.3	4.6	5.0	4.6	5.12	3.6	5.1	...	...
7	6.2	4.3	4.8	5.0	4.2	5.2	3.8	5.0	3.7	6.4

NUMBER OF CULTURE	65 DAYS		86 DAYS		100 DAYS		114 DAYS	
	pH	Available P	pH	Available P	pH	Available P	pH	Available P
		per cent		*per cent*		*per cent*		*per cent*
1	3.2	17.6	3.2	19.1	3.0	24.9	2.6	31.7
2	3.2	15.9	3.2	19.0	2.8	25.1	2.8	28.4
3	3.4	16.0	3.4	18.0	3.0	24.0	3.0	26.7
4	3.8	14.6	3.8	16.7	3.8	20.1	3.8	20.4
5	3.8	14.5	3.8	15.9	3.2	20.4	3.2	20.6
6	...	...	...	...	...	...	...	...
7	3.8	15.4	4.0	16.1	3.2	21.8	3.2	21.6

to be explained. The added sulfuric acid, it might seem, reacts with the tricalcium phosphate liberating the dicalcium and monocalcium phosphates, and thereby gives these cultures a start. That the case is not so has been shown by the results presented in table 3. It seems that the acid instead of

attacking the tricalcium phosphate was absorbed or adsorbed by the so-called inert material, the soil.

What effect will the addition of sulfuric acid have on the microbial flora harboring the mixtures? No definite answer can be given and only postulates may be advanced, postulates based on the general principles of our knowledge in microbiology. It is known that different groups of organisms and species in the same group differ in their tolerance toward the reaction of the media. A detailed discussion of this question may be found in the paper of Waksman and Joffe (11). It is probable that the addition of small amounts of acid eliminated from the field undesirable competitors, and gave free range to the sulfur oxidizers. The rise in the hydrogen-ion concentration of the first three cultures seems to substantiate the advanced postulate. On the other hand, greater amounts of sulfuric acid seem not only to kill most of microbial flora, but even shock the strongest sulfur oxidizers. The sulfur-oxidizing bacteria will tolerate a reaction in sulfur-floats-soil mixtures as low as the pH 1.0, or lower. Pure cultures of a strong oxidizing bacterium reported by the writer (5) developed in a culture medium an acidity that required, for neutralization, 8.3 cc. of 0.1*N* NaOH per cubic centimeter of medium. These organisms were viable and upon transfer into favorable culture medium developed and functioned. The same organism when placed in a medium adjusted with sulfuric acid to a pH = 1.0 in some cases refused to grow and in other cases developed but very slowly. Lipman and Joffe (7) have shown that sulfur oxidation goes on rapidly in mixtures of 5 gm. of sulfur, 15 gm. of floats and 100 gm. of soil. The rôle of the latter in these mixtures is still obscure. The sulfur oxidation goes on rapidly. Because of the rapidity of oxidation, the possible influences in the competitive struggle of the microbial flora are obliterated. The amount of the soil is important because of its absorbing and adsorbing power. Under the conditions of the experiment reported in this paper, the addition of small amounts of acid seem to benefit sulfur oxidation.

COURSE OF CONVERSION OF INSOLUBLE PHOSPHATES INTO SOLUBLE PHOSPHATES IN SULFUR-FLOATS-SOIL MIXTURES

It has been pointed out that there are two sets of reactions involved in the process of making phosphates available by composting sulfur-floats-soil mixtures, that of sulfur oxidation and that of the action of sulfuric acid on floats. The reactions involved in the conversion of raw rock phosphate into soluble forms by means of acids belong to the type of reactions of *heterogeneous* systems. The rock phosphate minerals have no definite composition and the products formed are not always definite. In such *heterogeneous* systems the speed of the reaction is a function of a greater number of variables than in the case of a homogeneous system. According to Kazakow (b), there are factors which are common to both systems and they are:

1. Concentration of the reacting mass
2. Temperature of the reacting medium
3. Amount of contact of the reacting substances
4. Speed of diffusion of the reacting substances
5. Catalytic agents

Besides these factors we have others in a heterogeneous system where solid solution phases occur. These are:

6. Size of contact surface[3]
7. Chemical composition of the solid phase
8. Physical properties of the solid phase
9. Influence of formation of a solid phase as a result of the reaction

Factors 7 and 8 have a tremendous influence on the speed of the reaction and they are the least known, since the chemical make-up of the rock phosphate is still obscure. Kazakow (6) formulates the reactions involved in the formation of soluble phosphates as follows:

TREATMENT	RESULTS	
	Liquid phases	Solid phases
1. H_2SO_4 added in excess...	H_3PO_4, H_2SO_4, sulfates of Ca, Al, Fe	$CaSO_4 . 2H_2O$
2. Close to optimum	H_3PO_4, sulfates of Ca, Al, Fe	$CaSO_4 . 2H_2O$
3. Optimum.....	H_3PO_4, sulfates of Ca, phosphates of Al and Fe	$CaSO_4 . 2H_2O$
4. Not enough acid.....	H_3PO_4, sulfates of Ca, phosphates of Ca, Al and Fe	$CaSO_4 . 2H_2O$ and part of undissolved phosphate

In the acid phosphate, or super-phosphate industry the idea is to obtain monocalcium phosphate and for convenience the reaction is represented as follows:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = CaH_4(PO_4)_2 + 2\,CaSO_4 . 2H_2O.$$

As it may be deduced from the scheme presented by Kazakow enough acid has to be used to accomplish this reaction; the practice is to use acid containing about 30 to 38 per cent of water (chamber acid of 50° B), since much water is necessary for the gypsum formation.

In the case of the sulfur-floats-soil mixtures, the amount of sulfuric acid formed at any moment is small and in the presence of the large amounts of tricalcium phosphate no accumulation of acid is possible; the reactions are slowly approaching equilibrium and coming to completion. The transition

[3] The size of the particles of the rock in the manufacture of acid phosphate has a tremendous influence. Theoretically, all other conditions being equal, the speed of solution of a solid in a liquid is proportional to the contact surface, and in spherical bodies (as we suppose in fine floats) the surface is proportional to the square of the radius. Particles with a radius of 0.1 mm. will dissolve twenty-five times as fast as particles with a 0.5 mm. radius.

stages are drawn out, e.g., the conversion from the tertiary to the primary phosphate is slow, since there is never an excess or a rapid formation of sulfuric acid. In a liquid medium where pure cultures of the sulfur-oxidizing organism were used (5) the steps involved in the transformation of the tertiary to the primary phosphates may easily be followed. The conditions in the culture medium are ideal for sulfur oxidation and the transition stages are short, e.g., the secondary phosphates quickly come to equilibrium with the tertiary

TABLE 4

Sulfur oxidation in a liquid medium

AGE OF CULTURE	NUMBER OF CULTURE	pH	SOLUBLE PHOSPHORUS PER 100 CC. OF MEDIUM*	AGE OF CULTURE	NUMBER OF CULTURE	pH	SOLUBLE PHOSPHORUS PER 100 CC. OF MEDIUM*
days			*mgm.*	*days*			*mgm.*
1	1	5.4	45.94	9	12	2.7	87.44
	2	5.4	45.39		14	2.7	95.16
	3	5.4	45.39		15	2.6	93.56
2	4	5.4	42.46	11	18	2.8	84.68
	5	5.4	42.75		19	2.6	101.25
3	6	5.3		13	20	2.3	183.51
	7	5.3	47.20		21	2.3	189.08
5	8	5.2	49.15	15	22	2.3	200.22
	9	4.0	60.80		23	2.3	206.70

* The total amount of phosphorus in 100 cc. of medium was 217.8 mgm.

phosphate and allow a rapid formation of the primary phosphate. The data recorded in table 4 demonstrate this point. The medium used was of the following composition:

	gm.
K_2HPO_4	1.00
$MgSO_4$	0.50
KCl	0.50
$FeSO_4$	0.01
$(NH_4)_2SO_4$	2.00
Sulfur	10.00
$Ca_3(PO_4)_2$	10.00

The medium was distributed in 250–cc. Erlenmeyer flasks and sterilized in flowing steam for ½ hour each day for 3 consecutive days. A series of flasks was inoculated and incubated at 27°C. Every day two or three flasks were taken out and analyzed for the hydrogen-ion concentration and soluble phosphates.

The interesting point of these data is that the crucial reaction for the conversion of the insoluble phosphates into soluble phosphates is that obtaining at

a hydrogen-ion concentration pH 2.7. It was apparent that at this point the primary phosphate was formed, which reacted with the tertiary, formed secondary and, in combination with the sulfuric acid constantly being formed in the cultures, completed the reaction. The transformation of the phosphates beginning at the pH = 2.7 went on very rapidly and within 4 days almost all of the phosphates have been made soluble. It is interesting to point out that the hydrogen-ion concentration of the chemically pure monobasic calcium phosphate and that of commercial acid phosphate is 2.6–2.7. When we examine the cultures of the sulfur-floats-soil mixtures in the aeration work and investigate the course of the reaction we also find that the reaction goes down to a pH 2.8–2.6 and remains at this point for a long time, contrary to what is happening in the liquid cultures. It seems that the amount of the monobasic salt formed is very small and it takes time for the reaction to come to completion. The driving force of the reaction is the sulfuric acid and the speed of its production by the microörganisms thus determines the velocity of the reaction.

It is known that fluorides are present in almost all phosphate rock, usually as calcium fluoride. The latter reacts with sulfuric acid, giving hydrogen fluoride and calcium sulfate as shown in the equations:

$$CaF_2 + H_2SO_4 = 2\ HF + CaSO_4$$

The hydrogen fluoride is a strong reagent and reacts with the silicates of the phosphate minerals forming silicon tetrafluoride:

$$4HF + SiO_2 = SiF_4 + 2H_2O$$

The gaseous silicon tetrafluoride is decomposed by water forming hydrofluosilicic acid and precipitating pure silica:

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$$

In the process of making acid phosphate most of the silicon tetrafluoride escapes and to a certain extent is beneficial to the process, since it makes the mixture more porous. The presence of this gas could be detected by its well known penetrating odor in the sulfur-floats-soil mixtures, especially when the sulfur-oxidizing organisms were active. The effect of this gas on the pure cultures of the sulfur-oxidizing microörganisms has not yet been studied. In mixtures with only 15 per cent of rock phosphate, 100 per cent conversion of the insoluble phosphates into soluble phosphates has been accomplished in 7 and 8 weeks, and in such cases, the odor of the silicon tetrafluoride was at times very strong.

This seems to indicate that the gas has no deleterious effect on the organisms. Still a more detailed study with the pure organisms is to be taken up, before any definite statement can be made. The other constituents of the minerals of rock phosphate undoubtedly play their part. With all the handicaps and

unknowns in the process, in the case of the aeration study as shown in table 1, 50 per cent of the phosphates has been made available.

One point is to be remembered in making analysis for the soluble phosphates: the total phosphates must be determined every time, since the percentage of the total will vary in the sample, for the oxidation of the sulfur, as shown in the earlier part of this paper, increases the weight of the mixture. It will therefore decrease the percentage of total phosphorus while the soluble phosphates will increase proportionally. This point has been overlooked in the earlier work at the New Jersey Agricultural Experiment Station as well as by workers of other stations.

The problem of making acid phosphate by the Lipman process of mixing rock phosphate, sulfur and soil is therefore chiefly a problem of providing ideal conditions for the sulfur-oxidizing bacteria. The different environmental conditions, variation of treatment, effect of temperature, inoculation and many other factors will be taken up in another paper. It will be shown that making phosphates available by the Lipman process has tremendous possibilities. In certain cropping systems this process will replace acid phosphate.

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THE ORGANIC PHOSPHORUS CONTENT OF SOME IOWA SOILS

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The form in which phosphorus occurs, as well as its function in soils has been the subject of much study. Many years ago it was suggested that part of the phosphorus in soils occurs in an organic form, but some investigators doubted the occurrence of sufficient amounts to be of any significance. Various methods of determining the mineral phosphorus compounds in soil have been suggested, but it is only comparatively recently that a method has been developed which serves to distinguish between organic and inorganic phosphorus, and to show that there is an appreciable amount of the former in most soils. Potter and Benton (6) first attempted to determine organic phosphorus in soil and they devised a method which proved quite satisfactory. Schollenberger (7) studied the problem later and modified the method slightly. His conclusions agreed with those of Potter and Benton, however, in showing that there is a rather large amount of soil phosphorus in the organic form. Very little work has been done as yet to show the relationship of organic phosphorus to other constituents of the soil and to the fertility of particular soil types. It would be very desirable to know the relation organic phosphorus bears to fertility. Is it more or less available to plants than inorganic phosphorus? Does organic phosphorus revert to the inorganic form and how rapidly? These, and many other questions remain to be answered when more is known about the organic phosphorus content of soils.

A review of the literature shows that as early as 1844 Mulder (1) noted the presence of phosphorus in organic soil material.

Schmoeger (2) studied the effect of igniting soil and of heating with water under pressure, and concluded that the increased solubility of phosphorus in hydrochloric acid after ignition was due to the destruction of insoluble organic phosphorus compounds. He concluded that the phosphorus was in the form of nuclein or similar compounds.

Hopkins and Pettit (3) noted that certain soils showed a uniform mineral composition in surface, subsurface, and subsoil, and suggested that the difference in phosphorus in surface and subsoil might be due to organic phosphorus. They suggested a method for calculating organic phosphorus.

[1] The author wishes to acknowledge his indebtedness to Dr. P. E. Brown for suggestions and criticisms in preparing the manuscript.

Stewart (4) discussed the solubility of soil phosphorus in hydrochloric acid and ammonia and concluded that the greater part at least of the ammonia-soluble phosphorus is organic.

Fraps (5) showed that inorganic phosphates were soluble in ammonia after ignition and extraction with hydrochloric acid. He concluded that no method previously advocated would distinguish between organic and inorganic phosphorus in ammonia extracts.

Potter and Beuton (6) originated a method for distinguishing between organic and inorganic phosphorus in ammonia extracts.

Schollenberger (7) developed further the method of Potter and Benton and he discussed the relationships between organic phosphorus and other constituents. He concluded that organic phosphorus and nitrogen exist in the same ratio at different depths.

EXPERIMENTAL

The object of this paper is to describe some preliminary experiments in a study of the organic phosphorus content of several Iowa soils.

The four soils used were selected so as to give as wide a range of conditions as possible and are described below.[2]

No. 1. Wabash silty clay loam. "A dark brown to black silty clay loam to a depth of 18 inches, becoming somewhat lighter in color at that point. A dark brown to lighter brown silty clay loam to silty clay or clay to a depth of 36 inches. The soil is level and often poorly drained." The organic matter content is very high. Both surface and subsoil are low in lime. This soil when properly drained and worked is capable of very high productivity. This soil in its native condition may, in spite of its poor drainage and low bacterial activity, be said to possess high latent fertility.

No. 2. Clinton silt loam. "The surface soil is a light brown to grayish-brown silt loam. This extends to a depth of 8 to 12 inches at which point it grades into a layer of yellowish-brown or yellowish-gray silty clay mottled with yellowish-brown. This intermediate layer is usually 4 to 8 inches in depth and changes abruptly into a yellowish-gray silty clay mottled with yellowish-brown and rusty brown. This subsoil is very plastic when wet and compact and hard when dry." The drainage is good, but the soil washes badly. The organic content of the soil is low. The phosphorus content is comparatively low and the soil reaction is acid.

No. 3. Hancock silty clay. "The surface soil is only 4 to 6 inches in depth, and the subsoil extends to 12 to 15 inches giving way below to a gray and brown mottled or drab plastic clay which extends to 3 feet or more." The soil is rather high in total phosphorus and low in organic matter.

No. 4. Jackson silt loam. "The surface soil is a light-brown, smooth, silt loam to a depth of 8 to 12 inches and passes into a yellowish-brown silty clay loam to silty clay. The subsoil is rather compact." The application of lime where the soil is acid and of phosphorus and organic matter gives good results. This particular soil was selected because of its low phosphorus and organic carbon content and because of its acidity and low fertility.

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[2] Quotations are taken from Soil Survey Reports of Iowa: Soil No. 1, Wright County Soils (in press); Soil No. 2, Johnson County Soils (in press); Soil No. 3, Pottawattamie County Soils; Soil Survey Report No. 2; Soil No. 4, Henry County Soils; Soil Survey Report No. 15.

No. 1. High organic carbon, phosphorus, and nitrogen, high latent fertility.
No. 2. Low nitrogen and organic carbon, relatively high total phosphorus.
No. 3. High total phosphorus and low organic carbon, high nitrogen.
No. 4. Low phosphorus, carbon and nitrogen, low fertility.

The analytical data given in table 1 with the exception of those giving organic phosphorus are taken from the analyses made in connection with the work of the Iowa Soil Survey.[3] The organic phosphorus results were obtained by the method developed by Schollenberger with some slight modifications. This method involves the preliminary extraction of the soil with 1 per cent HCl followed by the extraction of the phosphorus by eight hours shaking with 4 per cent ammonia. After the extraction with HCl, the soil was washed free

TABLE 1

Analyses of soils

SOIL STRATUM	ORGANIC CARBON	NITROGEN	PHOSPHORUS	ORGANIC PHOSPHORUS
	lbs. per acre	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*
Soil 1:				
Surface	129,354	9,500	1,563	393.46
Subsurface	178,542	9,760	2,398	482.40
Subsoil	116,298	6,180	2,304	690.36
Soil 2:				
Surface	20,256	1,500	1,428	72.22
Subsurface	12,448	1,000	2,560	
Subsoil	18,509	1,320	3,072	233.82
Soil 3:				
Surface	52,428	4,380	1,900	289.40
Subsurface	73,016	6,800	3,120	422.80
Subsoil	63,834	6,600	4,260	623.40
Soil 4:				
Surface	26,880	2,376	830	289.40
Subsurface	21,960	2,123	1,278	267.40
Subsoil	23,280	2,433	2,124	345.18

from chlorides, dried and ground to pass thru a 100-mesh sieve. 75 gm. were shaken with 750 cc. of 4 per cent ammonia. The soil suspension was set aside to settle then filtered through porcelain filters under 45 pounds pressure. This method of separation is open to some objection because it has been found that part of the organic matter does not pass through the filter. However, there was no difficulty experienced in the filtration. Soil no. 1 with the highest organic matter content filtered more slowly, but in every sample all but a few cubic centimeters filtered through. If there were any great discrepancy in results due to the filtration it should show up in soil no. 1. Here, however,

[3] The soil survey of Iowa is carried out by the Soils Section of the Iowa Agricultural Experiment Station in cooperation with the Bureau of Soils of the United States Department of Agriculture.

there was found a high percentage of organic phosphorus. Fraps (8) found with pure humic acid as much as 10 per cent loss in filtration. Schollenberger in comparing total phosphorus in an original ammonia soil extract with one filtered through unglazed porcelain found 6.6 per cent loss. Granting a loss of 10 per cent, the differences in percentages of organic phosphorus in the soil types used was so great that the value of the comparisons is not lost. In following up this preliminary work, however, a method of separation will be used which will eliminate this factor of loss.

Total phosphorus was determined from a 100 cc. portion of the filtrate. Inorganic phosphorus was determined from an equal aliquot. Organic

TABLE 2

Ratios of various constituents

SOIL STRATUM	NITROGEN-CARBON RATIO	ORGANIC PHOSPHORUS-TOTAL PHOSPHORUS RATIO	ORGANIC PHOSPHORUS-ORGANIC CARBON RATIO	ORGANIC PHOSPHORUS-NITROGEN RATIO
Soil 1:				
Surface	1–13.6	1– 3.98	1–328.7	1–24.1
Subsurface	1–18.3	1– 4.97	1–370.1	1–20.2
Subsoil	1–18.6	1– 3.34	1–168.4	1– 8.9
Soil 2:				
Surface	1–13.5	1–19.84	1–280.4	1–20.7
Subsurface	1–12.4			
Subsoil	1–14.0	1–13.15	1– 79.2	1– 5.6
Soil 3:				
Surface	1–11.9	1– 6.57	1–181.1	1–15.1
Subsurface	1–10.7	1– 7.40	1–172.6	1–16.0
Subsoil	1– 9.6	1– 6.84	1–102.3	1–10.5
Soil 4:				
Surface	1–11.3	1– 2.87	1– 92.8	1– 8.2
Subsurface	1–10.3	1– 4.80	1– 82.1	1– 7.9
Subsoil	1– 9.5	1– 6.17	1– 67.7	1– 7.0

phosphorus was obtained by taking the difference. All determinations were run in duplicate. It will be noted that in some cases rather large proportions of the total phosphorus were in organic form.

DISCUSSION OF RESULTS

Table 2 gives the calculations of the nitrogen-carbon, organic phosphorus-total phosphorus, organic phosphorus-organic carbon, and organic phosphorus-nitrogen ratios. By examining this table it may be seen that the nitrogen-carbon ratio is wider in soil no. 1 than in any of the other soils. This is as might be expected since soil no. 1 contains much more organic matter than any of the other soils. There has been less cropping on this soil than on the average upland soils of this section, drainage is poor and aeration deficient; hence organic matter has accumulated. Soil no. 4 shows the narrowest ratio;

and although it is very little different from no. 3, more decomposition and greater loss of easily decomposed organic matter has evidently occurred in this type.

When the ratio of organic phosphorus to total phosphorus is observed some interesting comparisons will be noted. For instance, the soil having the highest latent fertility (soil no. 1) and the soil having the lowest latent fertility (soil no. 4), show the highest ratios of organic phosphorus to total phosphorus. However, it is not fair to compare these two soils from the phosphorus standpoint alone since soil no. 1 is well supplied with nitrogen and has nearly twice as much total phosphorus. The significant part of the comparison is that a soil like no. 4 which is comparatively low in fertility and with so low a total phosphorus content should have 34 per cent of its phosphorus in organic form. This seems to indicate that organic phosphorus is perhaps less available than inorganic and remains in organic form rather tenaciously. In soil no. 4 if organic phosphorus were readily changed to inorganic it would hardly be expected that so large a percentage of organic phosphorus would be found. Following this line of reasoning it would be expected that soil no. 2 with only 5 per cent organic phosphorus would show a greater response to nitrogen than to phosphorus, since it has only 1500 pounds of nitrogen and has a comparatively high amount (1428 pounds) of total phosphorus of which only 5 per cent is organic.

Table 2 shows that with the exception of soil no. 4 the ratio of organic to total phosphorus is fairly constant at all depths. Soil no. 4 has evidently lost more of its inorganic phosphorus.

The organic phosphorus-nitrogen ratio shows a very striking contrast to the organic phosphorus-total phosphorus ratio. There is a wider ratio in the surface soils in all cases than in the subsoils in the former. This indicates that the nitrogen accumulated at the surface and made soluble has been leached out more rapidly than has the organic phosphorus. This of course is not surprising.

It may readily be seen from table 2 that the ratios of organic phosphorus to organic carbon are so different that no one ratio will serve for calculating organic phosphorus from organic carbon in different soil types. There is a range in ratios in surface soils from 1 to 328.7 in soil 1, to 1 to 92.8 in soil 4. However, if a large number of determinations had been made on each type it is possible, though not probable, that a more satisfactory and uniform ratio might have been secured.

Table 3 shows the amounts in all soils at different depths based on 2,000,000 pounds for surface, subsurface and subsoil. It is interesting to observe that organic phosphorus is rather uniform in subsurface and subsoil in all cases. Unfortunately the subsurface determination of soil no. 2 was lost.

The only explanation which can be suggested for this is that the organic phosphorus in the soil, or the phosphorus called organic, seems to remain as such and is rather uniformly distributed throughout the soil with the exception

of the surface where the amount has been increased by decaying plant residues.

No attempt has been made to draw any conclusions from these few analyses. This paper is merely a preliminary report on the problem. The results are interesting and indicative of the need of further study of organic phosphorus, but they will not permit of definite conclusions.

TABLE 3

Organic phosphorus in soil on basis of 2,000,000 pounds of soil for surface, for subsurface, and for subsoil

SOIL STRATUM	ORGANIC PHOSPHORUS
	lbs.
Soil 1:	
Surface	393.46
Subsurface	241.20
Subsoil	230.12
Soil 2:	
Surface	72.22
Subsurface	
Subsoil	77.94
Soil 3:	
Surface	289.40
Subsurface	211.40
Subsoil	211.70
Soil 4:	
Surface	289.40
Subsurface	133.70
Subsoil	115.09

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SOME EXPERIMENTS ON RECLAMATION OF INFERTILE ALKALI SOILS BY MEANS OF GYPSUM AND OTHER TREATMENTS

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The experiments reported here were made during the year 1920 in the hope of finding out as quickly as possible what might be accomplished to restore fertility by simple treatments to the alkali soils of the University Farm at Kearney Vineyard near Fresno, California. Some of these soils had once been capable of producing excellent crops, but have now become so filled with alkali that little of value will grow on them. The immediate object of these experiments was to determine what kind of treatments should be tried in the fields to restore fertility to these alkali soils.

During the years 1914–18 the Experiment Station had endeavored to reclaim an area of 160 acres of this land known as the Experimental Drainage Tract. A system of tile drains was installed, the land was flooded, and thus a large amount of saline and alkaline matter was removed in the drainage. Yet the land was not permanently reclaimed. Much of it remained bare, or covered only with alkali weeds.

At a conference at the University in August, 1919 it was decided to make a detailed survey to determine the extent and nature of the alkali. After the tract had been mapped, a ton or more of soil from each of five localities representing the chief variations in alkalinity was brought to the laboratory for experimental study. The soils were air-dried, screened and thoroughly mixed, then stored in closed bins in the house.

THE CHARACTER OF THE SOILS

There is considerable variation in the physical character of these soils, but in general they are classed as Madera fine sandy loam. No. 15 is a fertile, non-alkaline soil taken from the grove of ornamental trees. It was used as a check or standard to show what might be expected from a similar soil which contained no alkali.

In respect to alkali these soils beginning with the worst, may be described as follows:

No. 16 is a strongly alkaline and saline soil from area 118 of the Experimental Drainage Tract, section 6. It is devoid of any vegetation.

No. 17 was originally a similar soil from area 58 of the Experimental Drainage Tract but it had been leached in the field and later cropped. Leaching had removed the alkali and

salts so that it contains less than one-fourth as much as soil 16, but it is still very toxic and unable to support vegetation.

No. 18 is a highly saline but not alkaline soil from the olive orchard. It is too saline to permit much growth of crops.

No. 19 is a moderately alkaline and saline soil from area 200 on North Monarch Vineyard. It supports a moderate growth of barley.

No. 20 is a similar soil from the same locality, but is more alkaline, and highly saline. It is very infertile.

The general composition and qualities of these soils are indicated in tables 1 and 2. They show that the soils are similar in ultimate composition. The chief variations are in Na, Cl, SO_4 and CO_3, which are the characteristic constituents of alkali soils. These differences are more apparent in the water extracts, especially in those made with carbon-dioxide-free water.

THE VARIOUS TREATMENTS

Originally it was intended to treat the soils only with gypsum in varying amounts. Later it was seen that gypsum was not effecting the restoration of these soils to productiveness. Accordingly, as opportunity offered, various other procedures were tried, but only to a very limited extent on account of lack of time and facilities. The leaching of soil 18 should be regarded as a separate experiment, as this soil was not alkaline.

The soils varied greatly in alkalinity and in salinity, hence all were not treated alike. Soils 16 and 17 were so highly alkaline that it was hardly expected to restore fertility in them by gypsum alone, so only one pot of each treatment was prepared. It was hoped that some amount of gypsum would improve soils 19 and 20 so that they would produce a crop, hence each treatment was tried in seven pots, in order to obtain somewhat average or representative results.

The gypsum treatments of soils 16 and 17 were made by G. R. Stewart about three months previous to the time the treatments on soils 18, 19 and 20 were started. The treatments for the latter soils were decided upon at a conference between Professors J. S. Burd and D. R. Hoagland and the writer.

The gypsum, or other added material, was mixed with the dry soil, then the mixture was placed in 5-gallon earthenware jars and watered. After a few days barley was planted in the jars.

Soils 16 and 17 were treated alike with gypsum ($CaSO_4 2H_2O$) in amounts from 500 to 80,000 pounds per acre.

Soil 18, saline not alkaline, was leached only.

Soils 19 and 20 were treated with gypsum in amounts of 3000 to 64000 pounds per acre.

Organic treatments

One jar each of soils 16, 17, 19, 20 was mixed with 1 per cent of its weight in rotted manure; one jar of each with 1 per cent in alfalfa meal; and one of each with 2 per cent in lawn (blue-grass) clippings. These were planted and cared for like the gypsum treatments.

The leaching treatments

Soil 18 was the only one extensively treated by leachings.

This very saline, but not alkaline soil required only leaching to remove the excess of salts in order to restore fertility. Two qualities of water were used; first, the ordinary tap water.

TABLE 1

Composition of the water extracts of alkali soils

Ratio of soil to water—1:5

SOIL CONSTITUENTS	QUANTITIES FOUND IN SAMPLES EXPRESSED AS PARTS PER MILLION IN DRY SOIL				
	No. 16	No. 17	No. 18	No. 19	No. 20
Extract made with ordinary distilled water, filtered on Pasteur filter					
	p. p. m.	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*
Total solids	26,695	6,128	8,173	2,296	4,934
Ca	61	25	450	31	26
Mg	7	8	169	8	9
Na	9,682	2,046	1,545	707	1,670
K			116		
SO_4	1,807	822	677	509	550
NO_3			1,624	112	329
CO_3	2,457	302	0	0	0
HCO_3	4,995	983	259	499	504
Cl	7,988	1,663	1,444	611	1,681
Extract made with distilled water free of CO_2, filtered on paper					
CO_3	3,300	600	0	48	120
HCO_3	3,050	610	61	238	183
Cl	7,600	1,850	1,275	635	1,825

TABLE 2

*Composition of acid extracts of alkali soils**

SOIL CONSTITUENTS	QUANTITIES FOUND IN SAMPLES EXPRESSED AS PERCENTAGES OF DRY SOIL.				
	No. 16	No. 17	No. 18	No. 19	No. 20
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
Insoluble residues	88.43	89.78	77.98	88.54	88.80
Soluble silica	0.42	0.46	0.50	0.51	0.45
Fe	1.97	2.05	3.42	2.31	2.01
Al	1.24	1.21	4.31	1.64	1.69
Ca	0.91	0.80	0.90	0.81	1.04
Mg	0.45	0.45	0.51	0.44	0.41
Na	1.13	0.41	0.29	0.22	0.18
K	0.52	0.57	1.34	0.65	0.35
SO_4	0.20	0.08	0.15	0.06	0.04
PO_4	0.06	0.05	0.05	0.04	0.09
Cl in water extract	0.80	0.17	0.14	0.06	0.17
Organic, loss, water, etc.	3.33	3.79	10.18	4.64	4.62
Total CO_2 by evolution	0.54	0.18	0.07	0.07	0.12
Acid Equivalent = $\%H_2SO_4$ required to neutralize	0.98	0.31	0.015	0.088	0.157
Hydrogen Ion Concentration of moist soil (pH)	9+	9+	7.0	8.2	8.6

*Extract made according to method of Association of Official Agricultural Chemists, HCl specific gravity 1.115, 10 hours in steam bath.

Calcium and magnesium bicarbonates constitute the chief soluble ingredients of this water. It was considerably superior to the synthetic water no. 1 in facility of leaching, and left the soil in better physical condition. Barley seemed to do better on the soil leached with tap water.

Sodium carbonate (20 p.p.m.) is the characteristic constituent of synthetic water no. 1 used to leach the duplicate lot of soil 18. This water tended to puddle the soil and percolated much more slowly than the tap water. Long use of such a water for irrigation might be expected to produce an alkali soil.

It is thought that the tap water was superior on account of its content of calcium which maintained floculation of the soil.

The procedure employed was as follows:

Fifty pounds of soil was placed on muslin cloth in a large galvanized filter 2½ feet in diameter. The soil made a layer 1¼ to 2 inches thick. A nearly equal volume of water, 8 liters, was added and allowed to run through. Then 8 liters more were added; after it ran through, 8 liters more. After this, suction was applied for several hours until no more water was removed. Then the soil was taken out, spread on paper and left in a warm room until dry. Later it was pulverized and mixed and returned to the jars.

A few leachings were made on soil 16. One lot leached with distilled water containing 0.1 per cent gypsum was placed in jar 131. One lot was leached in a similar manner with synthetic water no. 1 containing 0.1 per cent gypsum. It was in two portions, one placed in jar 133 remained quite alkaline and saline. Enough sulfuric acid to neutralize the soil was added to the last leaching water applied to the other. Still retaining much saline matter, it was placed in jar 132. Barley germinated well in these soils, but died without making much growth. The physical condition of these soils was very bad. They were badly puddled, and not easily penetrated by water. This effect was generally observed after leaching a very alkaline soil.

Leaching in Glass Tubes

Although this was a separate experiment it is of interest in this connection to mention the results obtained.

The soils were placed in glass tubes about 1 inch in diameter, 4 to 5 feet long. The soil columns were about 4 feet long. They were leached with synthetic water no. 1 and no. 2. The tubes were too narrow and several of them broke so that results were unsatisfactory.

In general, the more saline water no. 2 percolated more rapidly than the alkaline water no. 1. After the larger proportions of the salts had been removed from soils 16 and 17, percolation very nearly ceased. On soils 19 and 20 percolation became very slow toward the last, but finally nearly all the salinity and most of the alkalinity was removed. These soils are much more easily leached than 16 and 17.

RESULTS OF SOIL TREATMENT

The crop of barley

Barley was the crop selected to indicate the effect of the treatments. The soils were placed in 5-gallon stone-ware jars, each holding about 50 pounds of soil. Seed was planted in January. During the time the crop was growing, the jars stood in an open shed with a glass roof, so that the soils were exposed to ordinary weather conditions except that rain was excluded. The moisture content was maintained near the optimum (15 to 18 per cent— by frequent additions of distilled water. After the crop had matured and dried, it was harvested and the weights of heads and of stalks recorded. Seven jars of the fertile soil 15 were used for checks and cropped in the same manner.

The crop produced is taken as somewhat indicative of the degree of improvement in the various soils consequent on the treatments applied.

Except in the case of one treatment only none of the seeds planted in soil 16 germinated. On some of the leached soils there was fair germination but very little growth. Soil 17 permitted some germination, but little crop. Soils 18 and 19 produced considerable crop as shown in table 3. Soil 20 allowed some germination, but the plants soon ceased to grow.

TABLE 3

Relative yields of barley on treated alkali soils

SOIL NUMBER	TREATMENT	YIELD OF HEADS AND STALKS		YIELD OF HEADS			
		Total weight	Comparison with "check"	Total weight	Comparison with "check"	Number of heads	Comparison with "check"
		gm.	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*
15	None (check).....	37.0	100	19.5	100	12.3	100
16	Gypsum, all amounts,....	*		*		*	
17	500 lbs. gypsum.....	3.0	8	0.5	3	2.0	16
17	32,000 lbs. gypsum...	11.5	31	3.5	18	5.0	40
17	80,000 lbs. gypsum	8.0	22	2.5	13	5.0	40
18	None.....	4.3	12	1.3	7	4.3	35
18	Leached, tap water.....	39.4	106	17.3	89	14.7	119
18	Leached, synthetic water.	33.6	91	16.9	87	13.3	108
19	None.....	7.2	19	3.9	20	6.0	48
19	2000 lbs. gypsum.....	9.1	25	5.1	26	7.9	64
19	8000 lbs. gypsum.....	12.0	32	6.9	35	10.6	86
19	16,000 lbs. gypsum.....	13.1	35	7.6	38	11.9	97
19	64,000 lbs. gypsum.....	16.1	44	9.5	48	13.0	106
20	Gypsum, all amounts....	†		†		†	

* No germination.

† Some germination, but no crop.

When the toxicity is sufficiently overcome by gypsum and leaching to permit a fair growth of crop, it appears that the plants bear an undue number and weight of heads in proportion to total weight. This may be due to the endeavor of the plant to reproduce itself under adverse conditions of nutrition.

Changes in alkalinity

Four or five weeks after the barley had been planted, when the effect of the alkali on the plants was evident, samples of soil were taken from both top and bottom of jars representing nearly all the different treatments.

TABLE 4

Effects of treatments on soil

SOIL	TREATMENT	pH VALUE OF SOIL EXTRACT	H_2SO_4 REQUIRED TO NEUTRALIZE 1-10 EXTRACT BY		H_2SO_4 REQUIRED TO NEUTRALIZE, MUD SUSPENSION	CHLORINE
			Phenolphthalein	Methyl orange		
	per acre		*per cent**	*per cent**	*per cent**	*per cent**
No. 15						
Top	None	6	0.000	0.014	0.000	0.006
Bottom	None	6	0.000	0.010	0.000	0.010
No. 16						
Original	None	9+	0.255	0.745	0.98	0.78
Top	1000 lbs. gypsum	9+	0.274	0.676		0.68
Bottom	1000 lbs. gypsum	9+	0.290	0.764		0.68
Top	8000 lbs. gypsum	9+	0.235	0.598		0.72
Bottom	8000 lbs. gypsum	8+	0.290	0.715		0.73
Top	80,000 lbs. gypsum	9+	0.050	0.120		0.57
Bottom	80,000 lbs. gypsum	9+	0.070	0.137		0.66
Top	Alfalfa	9+	0.220	0.510		0.46
Bottom	Alfalfa	9+	0.372	0.884		0.92
Whole jar	Leached and neutralized	6.5	0.000	0.016	0.010	0.01
Whole jar	Leached with gypsum	9+	0.027	0.059	0.137	0.00
No. 17						
Original	None	9+	0.059	0.176	0.320	0.15
Top	1000 lbs. gypsum	7.4	0.001	0.031		0.012
Bottom	1000 lbs. gypsum	8.8	0.012	0.057		0.350
Top	8000 lbs. gypsum	9+	0.023	0.074		0.076
Bottom	8000 lbs. gypsum	9+	0.015	0.104		0.224
Top	80,000 lbs. gypsum	8.5	0.008	0.033		0.050
Bottom	80,000 lbs. gypsum	9.0	0.029	0.059		0.276
Whole jar	Manure, 10 tons	9+	0.039	0.127		0.03
Whole jar	Grass clippings, 20 tons	9+	0.055	0.116		0.08
Top	Alfalfa	9+	0.015	0.113		0.02
Bottom	Alfalfa	9+	0.059	0.204		0.26
No. 18						
Original	None	7	0.000	0.016	0.015	0.134
Top	None	6.5	0.000	0.016		0.094
Bottom		6.5	0.000	0.016		0.180
Top	Leached with tap water	7.2	0.000	0.037		0.004
Bottom	Leached with tap water	6.8	0.000	0.026		0.012
Top	Leached with synthetic water no. 1	6.8	0.000	0.030		0.012
Bottom	Leached with synthetic water no. 1	7.2	0.000	0.034		0.006

* Per cent of the dry soil.

TABLE 4—*Concluded*

SOIL	TREATMENT	pH OF SOIL EXTRACT	H_2SO_4 REQUIRED TO NEUTRALIZE 1-10 EXTRACT BY		H_2SO_4 REQUIRED TO NEUTRALIZE, MUD SUSPENSION	CHLORINE
			Phenolphthalein	Methyl orange		
	per acre		*per cent**	*per cent**	*per cent**	*per cent**
No. 19						
Original	None	8.2	0.008	0.048	0.088	0.076
Top	None	8.8	0.010	0.051		0.020
Bottom		7.2	0.004	0.043		0.114
Top	2,000 lbs. gypsum	8.8	0.006	0.054		0.110
Bottom		7.2	0.000	0.025		0.156
Top	8,000 lbs. gypsum	6.8	0.000	0.029		0.020
Bottom		6.8	0.000	0.019		0.140
Top	16,000 lbs. gypsum	6.8	0.000	0.019		0.020
Bottom		6.8	0.000	0.019		0.100
Top	64,000 lbs. gypsum	6.6	0.000	0.019		0.030
Bottom		6.6	0.000	0.019		0.066
Top	Alfalfa	8.5	0.016	0.065	0.049	0.008
Bottom		8.5	0.008	0.069	0.049	0.170
No. 20						
Original	None	8.6	0.040	0.140	0.157	0.182
Top	None	8.8	0.020	0.064	0.074	0.160
Bottom		8.8	0.016	0.060	0.074	0.220
Top	8000 lbs. gypsum	7.2	0.002	0.036	0.037	0.220
Bottom		7.2	0.004	0.036	0.049	0.220
Top	16,000 lbs. gypsum	7.2	0.000	0.028	0.049	0.170
Bottom		7.8	0.000	0.028	0.025	0.280
Top	32,000 gypsum	6.8	0.000	0.024	0.037	0.124
Bottom		6.8	0.000	0.024	0.049	0.210
Top	64,000 lbs. gypsum	6.8	0.000	0.014	0.049	0.110
Bottom		6.8	0.000	0.026	0.049	0.220
Top	Alfalfa	8.8	0.030	0.090	0.074	0.110
Bottom		8.8	0.016	0.075	0.123	0.276

To determine the alkalinity of the soil two methods were used. In the first method, 1 to 10 water extract (CO_2–free water) was titrated with acid, with phenolphthalein and methyl orange as indicators; then Cl was determined by titration with $AgNO_3$ and chromate indicator. In the second method a suspension, or mud, containing 2 parts of soil to 1 part of water was titrated with 0.1 *N* H_2SO_4, the indicator being bromcresol purple on a white porcelain plate. Similar tests on the original soil are given for comparison. These data are shown in Table 4.

In general the table shows that gypsum reduced the total alkalinity and lowered the hydrogen-ion concentration somewhat in proportion to the amount added to the soil. In some of the mixtures there was much more gypsum than necessary to react with all the sodium carbonate in the soil. Also it is probable

that a large part of the gypsum in the higher applications did not react with the soda on account of lack of time and of sufficient water to dissolve the gypsum. Presence of calcium and sulfate in quantity, in the water extracts from the higher treatments of soils 17, 19 and 20, indicates that the gypsum had never been dissolved after being mixed with the soil. Only the highest application on soil 16 contained enough gypsum to neutralize all the soda in this soil.

The data also indicate that the soluble salts were largely removed from the top layers of soil in the jars and concentrated in the bottom during the first month after barley was planted. This undoubtedly enabled the grain to make a much better early growth than if such translocation had not taken place. It is probable that later in the period these salts migrated back toward the tops of the jars. The table also shows that the top soil in some jars had a higher hydrogen-ion concentration than the bottom. This seems to be a common effect of washing salts from an alkaline saline soil, and perhaps also from a non-alkaline soil.

The reaction between gypsum and sodium carbonate

There is usually a small amount of calcium in the water extract of most alkali soils, due to the solvent effect of sodium salts on calcium carbonate and also to replacement of calcium by sodium. But so long as the soil contains sodium carbonate enough to give it a hydrogen-ion concentration of pH-8.5 or higher, no considerable amount of calcium will be found in the water extract of the soil. This fact, together with the fact that gypsum is soluble in water only to the extent of about 0.25 per cent, sets a rather definite limit to the amount of alkali which can be neutralized by addition of gypsum to the soil without removal of the products of the reaction.

It might be thought that an excess of gypsum added to such a soil would gradually dissolve, as the reaction proceeded, so that if enough gypsum were present all of the sodium carbonate would be finally changed to sodium sulfate. But the tendency to reversal of this reaction in the presence of considerable amounts of sodium salts, is so great that it becomes impossible to neutralize large amounts of sodium carbonate in soil by gypsum, without leaching to remove the sodium sulfate. Examination of table 4 brings this out. Soils 16 and 17 did not become neutral by the addition of any amount of gypsum, though some of the applications were more than enough to combine with all the sodium carbonate present. The concentration of sodium salts was too great. On the contrary, soils 19 and 20 lost their alkalinity when treated with sufficient gypsum. But in this case the total concentration of sodium carbonate at the start was not greater than the equivalent possible concentration of gypsum in the soil solution. That is, the amount of gypsum which could dissolve in the soil solution at any one time was sufficient to react with all the sodium carbonate present. This did not restore fertility because the salinity of the soils was too great for vegetation.

Effects of the organic treatments

On March 11 and 12, after the barley had made a good growth but before heading, the carbon dioxide in the soil atmosphere was determined, with results shown in table 5. The air analyzed was drawn from the lower central part of the soil jars.

TABLE 5

Carbon dioxide in soil atmosphere after organic and other treatments

SOIL NUMBER	TREATMENT	CARBON DIOXIDE
		per cent
15	None	0.28
16	Gypsum, all proportions	0.23–0.40
16	Stable manure	0.23
16	Green manure	0.30
16	Alfalfa meal	0.46
16	Jar 133, leached	0.33
16	Jar 132, leached and acidified	0.35
17	Gypsum, all proportions	0.25–0.39
17	Stable manure	0.40
17	Green manure	0.80
17	Alfalfa meal	1.58
18	Original or leached	0.23–0.34
19	Gypsum, all proportions	0.27–0.45
19	Stable manure	0.37
19	Green manure	1.07
19	Alfalfa meal	0.71
20	None	0.28
20	Gypsum, up to 32,000 lbs.	0.23–0.34
20	Gypsum, 64,000 lbs.	0.50
20	Stable manure	0.47
20	Alfalfa meal	1.03
20	Green manure	0.90

In general, the more carbon dioxide in the soil air, the better was the growth of barley on any of the soils. Apparently gypsum had no considerable effect on the amount of carbon dioxide in this air, but organic matter increased it very much, according to the nature of the organic matter. Rotted manure, being relatively inert, was least effective, while the soils treated with alfalfa meal contained the greatest amount of carbon dioxide. The increased content of carbon dioxide lowered the intensity of alkalinity so that plants were able to grow in soil which, if untreated, permitted no growth.

For the purpose of starting an alkali-sensitive crop this means of reducing the intensity of alkalinity may be of great importance. After the delicate plants

have become sturdy, they usually will endure a higher degree of alkalinity such as would recur after the lowering of the carbon dioxide when the rotting organic matter has disappeared. But for permanent reduction of total alkalinity this method is of little value.

CONCLUSIONS

Excessive salinity, which renders a soil infertile, may be removed by simple leaching with water, so that the soil will again produce good crops as shown by soil 18.

Excessive alkalinity of a soil due to sodium silicate, carbonate or bicarbonate, may be ameliorated by gypsum, to some extent, but to restore fertility it is necessary to leach the soil after adding the gypsum.

Surface application of water to pots of soil may remove so much of the alkalinity, or more especially the salinity, to the lower levels of the jar that germination and growth of plants may take place in the top soil which otherwise would be quite toxic.

Increase of carbon dioxide in the soil atmosphere lowers the intensity of alkalinity and thus permits growth of plants otherwise impossible. Such increase of carbon dioxide is readily accomplished by decay of easily decomposed organic matter.

When a soil contains 0.5 per cent or more of sodium salts, including some sodium carbonate, it is improbable that it can be made fertile by addition of gypsum in any amount, because the reaction by which sodium carbonate is changed to sulfate tends to reverse, as shown in the equation:

$$Na_2CO_3 + CaSO_4 \rightleftarrows CaCO_3 + Na_2SO_4$$

In order to prevent this reversal it is necessary to remove the sodium salts by leaching or other adequate means. On account of the low solubility of gypsum (about 0.25 per cent) it is impossible to increase its concentration in the soil solution sufficiently to prevent reversal of the above reaction in the presence of much sodium salts.

It is not feasible to leach very alkaline soils without adding some flocculating agent, such as gypsum or calcium bicarbonate, in order to prevent puddling of the soil and interference with percolation.

Water of primary alkalinity, i.e. containing sodium carbonate or bicarbonate, is not well adapted to leaching alkali soils.

When sodium chloride or sodium sulfate is removed from a saline or from an alkaline-saline soil by leaching with water, the soil is likely to show an increased intensity of alkalinity, or lower hydrogen-ion concentration, before all the sodium carbonate is removed. This was observed with all the soils used in the experiment. The intensity of such induced alkalinity may be sufficient to be toxic to some plants, but the quantity will usually be so small that a moderate amount of carbon dioxide, such as the plant sets free or such as may be generated by decaying organic matter, will reduce the intensity to a point below the toxic limit.

CERTAIN RELATIONS BETWEEN THE PROTEIN CONTENT OF WHEAT AND THE LENGTH OF THE GROWING PERIOD OF THE HEAD-BEARING STALKS

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In another paper (1) the writer has shown how applications of soluble nitrogen, applied at certain growth phases of the plants, affected the protein content and hardness of "soft white" Australian wheat. A range from 8.6 to 15.2 per cent in protein and a range from no. 2 "soft white" to no. 1 "hard spring," according to commercial grading, represented the magnitude of differences in the quality of the wheat produced. Good correlation was obtained between the differences in protein content of the wheat and the time of nitrogen applications. The treatments are fully described in the paper cited.

Very marked differences in the time of tillering of the plants and culm formation were obtained by the treatments. Plants that produced tillers or culms early, produced soft wheat, low in protein; those that tillered late produced hard wheat, high in protein. Although a relationship could be shown between the time of tillering and the quality of the wheat, it does not appear that the important physiological condition affecting the protein content of the wheat is related, as the cause, merely to the time of tillering. The important physiological condition seemed to be the length of the growing period of the tillers as head-bearing stalks. The age of the plant when tillers arose was an important factor that affected the length of the growing period of the culms. Because the length of the growing period of wheat is relatively fixed for any given environmental complex, tillers that arose late in the growing period of the plant had a shorter span of growth than those that arose earlier. The differences obtained in the time of tillering depended largely upon the time when nitrogen was applied. In this respect, the time of application of nitrogen was a condition that affected the length of the growing period of the head-bearing stalks. That this was an important factor, or set of conditions, in the production of the wheats of varying protein content, is shown by table 1.

The table shows very clearly that the length of the growing period of the head-bearing stalks was decidedly shorter in those cultures that produced the high-protein wheat than it was in those that produced the low-protein wheat. The differences for the extreme cases were 68 days. The good correlations

apparent between the differences in protein content of the wheat with that of the length of the growing period of the stalks is strong indication that the two circumstances may be related as effect and cause, respectively.

As stated in the paper cited, the culture medium employed was a soil deficient in available nitrogen and had a low crop-producing power for cereals. It was a soil that responded very quickly in increased crop production upon receiving a moderate application of nitrogen. It was observed in this investigation that the cultures which received nitrogen at the time of planting the seed grew rapidly and soon developed the culms that became the head-bearing stalks. The cultures, because of the ample supply of available nitrogen, grew into strong plants. These decidedly exceeded all other cultures in vege-

TABLE 1

Relation between the protein content of spring wheat and the length of the growing period of the head-bearing stalks, as affected by applications of nitrogen at different growth phases of the plants

NUMBER OF TRIPLICATE JAR SERIES	DATE OF PLANTING	DAYS AFTER PLANTING WHEN N WAS APPLIED	COMMERCIAL GRADE	PROTEIN CONTENT	LENGTH* OF GROWING PERIOD OF HEAD-PRODUCING STALKS	TOTAL LENGTH OF GROWING PERIOD OF PLANTS
				per cent	*days*	*days*
1	1/14/19		2 soft white	8.6	193	201
2	1/14/19	17	2 soft white	9.3	187	197
3	1/14/19	33	1 soft white	10.4	167	194
4	1/14/19	48	2 hard spring	11.8	157	194
5	1/14/19	72	1 hard spring	13.2	140	206
6	1/14/19	110	1 hard spring	15.2	125	229

* Count was begun on the day branched leaves appeared which marked the inception of stalks and tillers.

tative development during the first four weeks of growth. When, however, the plants in the other pots received their applications of nitrogen later in the growing period, they responded to the treatment to a greater degree than did the cultures that received nitrogen at the time of planting, and exceeded them in growth. As a rule, the later the nitrogen was applied, the greater and quicker was the response in vegetative growth. This response in vegetative growth consisted primarily in the formation and rapid growth of tillers. Tillering was greater in all cultures that received nitrogen 33 days or more after planting than in those that received nitrogen earlier in the growing period. The maximum tillering of all the cultures was produced in those pots which received nitrogen 110 days after planting. Nearly all the tillers of all the cultures became head-bearing stalks. The condition, therefore, that initiated tillering, within the scope of the investigation, was, in a large measure, subject to change at will, while that of maturation of the plants which concluded the growth period was not so subject.

The table shows no correlation between the length of the growing period of the plants receiving different treatments and the protein content of the wheat. It is noted, however, that the cultures which received nitrogen 33 and 48 days after planting had the shortest growing period of all in the series. This shows that applications of nitrogen to wheat plants made at certain growth phases, can shorten the total length of the growing period, and applications of nitrogen made at other growth periods of the plant can lengthen its total growing period.

In view of the results obtained, the question may arise as to what the physiological causes are that relate the protein content of the wheat to the length of growing period of the head-bearing stalks. An answer to this question at present can be only in the nature of a suggestion. It is known that the protein and carbohydrate content of wheat, in general, may vary over a considerable range. This variation may be due to genetic characteristics of the plant, or to environmental conditions of growth. Apparently the latter set of factors as the cause of variation, is of much greater importance than the former. Differences in the protein and carbohydrate contents of the wheat, as found in this investigation, obviously imply that relatively different amounts of nitrogen compounds and carbon compounds were used in the processes of assimilation. The rate of absorption of nutrients and the length of the period of absorption, that is, the length of the growing period of the plant, are two factors among others that determine how much material can be absorbed. Both the total amount of nitrogen compounds and carbon compounds absorbed by the plant and their relative proportion one to the other, apparently were factors that affected the processes of assimilation and the kinds of products assimilated.

From the standpoint of rates of absorption, it is possible to conceive of two sets of conditions that would account for the high-protein wheat obtained in the investigation. One of these would be that the rate of carbon intake to that of nitrogen was decreased in the production of high-protein wheat as compared with that of low-protein wheat; the other that the rate of nitrogen intake to that of carbon was increased. Obviously the latter set of conditions seems the more probable of the two. It seems reasonable to assume that the plants that received the applications of nitrogen late, say from 48 to 110 days after planting, had a larger supply of this nutrient for their later growing period than did those plants that received nitrogen at the time of planting. The application of nitrogen made at the time of planting was partly used up by the vigorous growing plants at the time other cultures received their application of nitrogen. Consequently, when the application was made early in the growth period, there was not so much nitrogen available in the latter growth phases of the plants, when presumably the demand for this nutrient was the greatest, as was available in those cases where the nitrogen was applied late. While the supply of nitrogen available to the plants sets the limits of the amount that possibly may be absorbed, nevertheless, the capacity of the

plants to absorb and utilize the nitrogen presumably was an important factor that affected the rate of nitrogen intake. The condition of relative insufficiency of nitrogen under which the plants that produced the high-protein wheat were started, seemed to operate as a means that gave the plants a greater capacity to absorb and utilize the nitrogen when applied late. The larger total production of dry matter and the greater protein-content of the wheat obtained from plants that had a short growing period of the stalks was assumed to indicate the relatively larger capacity for nitrogen absorption and utilization.

The length of the period of growth during which nutrients are absorbed, is a factor that may affect the amount of material taken up by the plant. If the rates of absorption of nutrients had been the same for all plants throughout the growing period, then the plants that had a long growing period should, other conditions being equal, absorb a larger amount of nutrient material than those plants of a short growing period. So far as this may be applied to the carbon dioxide intake only, wheat of a long growing period would be expected to be more starchy than that of a short growing period, as in the former case it could build up more of the carbon photosynthetic products than in the latter. But the factor of the length of the period of growth does not explain the nitrogen relation as found in these different wheats. It thus seems that the most probable explanation of the cause of the differences in protein content of this wheat is to be found in the differences in the rates of absorption of nitrogen and its utilization, which were greater in the wheat whose head-bearing stalks had a short growing period than in those which had a long growing period.

REFERENCE

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